

MEASUREMENTS OF THE THERMAL CONDUCTIVITY OF SOME ORGANIC LIQUIDS

AND

A STUDY OF METHODS EMPLOYED FOR SUCH MEASUREMENTS

by

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ABSTRACT

The thermal conductivity of a few liquids is well established for a limited range of temperatures and pressures. The operating temperatures and pressures of industrial equipment are increasing rapidly for a number of reasons and the number of liquids being used for heat transfer media are also increasing. The need for additional, accurate thermal conductivity values over an extended temperature range are therefore required. The studies outlined in this thesis were directed towards making accurate determination of the thermal conductivity of organic liquids at temperatures up to 600°F and atmospheric pressure.

An exhaustive literature survey was made and a resumé of the investigations carried out by the more important researchers is summarized in tabular form. A number of empirical and theoretical expressions for the thermal conductivity of liquids are reviewed as well as the methods employed by a number of the many previous investigators. Invariably the method of determining the thermal conductivity of a liquid consisted of measuring the conductance of a layer of the liquid. The geometric arrangements of the apparatuses have been numerous and varied and the main criterion of their design has been the avoidance of convection and the isolation of the heat losses.

Two apparatuses, the hot-wire cell and the concentric cylinder cell, were selected as suitable apparatuses; the first for its simplicity and the second for the higher pressure determinations. Both cells

require the use of a constant temperature bath. For the temperature range and the accuracy required a suitable bath was developed. The result was an oil bath suitable for a temperature range from 80 to 250°F in which the measured temperature can be held within $\pm 0.002^\circ\text{F}$ for about one hour periods.

The hot-wire cell was used to determine the thermal conductivity of Carbon Tetrachloride and Toluene at atmospheric pressure for a temperature range from 70°F to their respective boiling points. Determinations were also made for two organic liquids, known as HE-40 and Hydrogenated Santowax OM, at atmospheric pressures and at temperatures up to 600°F.

The design of the cells and the bath is described in the thesis; the calibration and the use of the hot-wire cell are also completely documented. The values of the thermal conductivity determined for Carbon Tetrachloride and Toluene are compared to the most reliable results from the literature. Free convection is evident at the higher temperatures for the above fluids as well as for the organic fluids tested. The results are therefore considered unreliable and further work is required to isolate the effects of convection.

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NOMENCLATURE

- A = Surface area normal to heat flow.
- a = Thickness of the liquid layer.
- C = Velocity of propagation of the "phonon-gas".
- C_p = Specific heat at constant pressure.
- C_v = Specific heat at constant volume.
- d = Specific gravity at 60°F.
- d_f = Mean effective diameter of the filament.
- d_i = Inside diameter of the glass tube.
- d_o = Outside diameter of the glass tube.
- g = Acceleration due to gravity.
- H = Enthalpy of the "phonon-gas".
- K = Thermal Conductivity.
- K_g = Thermal conductivity of the Pyrex glass.
- L = Mean effective length of the test section.
- ℓ = Length of the mean freepath.
- M = Molecular weight.
- q = Heat transferred per unit time.
- R = Universal gas constant.
- r_i = Inside radius of the glass tube.
- r_f = Mean effective radius of the filament.
- r_o = Outside radius of the glass tube.
- T = Temperature.
- t = Time.
- T_b = Temperature of the bath.

T_f = Average temperature of the filament.

T_s = Melting temperature.

U = Velocity of sound in liquid.

V = Molar volume of the liquid.

\bar{V}_m = Mean molecular velocity.

V_s = Molecular volume.

x = Direction of heat transfer.

GREEK LETTERS:

β = Coefficient of thermal expansion.

ΔT = Temperature difference.

μ = Viscosity.

ν = Kinematic viscosity.

ρ = Density.

τ = Temperature interval.

Dimensionless Numbers:

$$\text{Grashof Number} \dots N_{GR} = \frac{g \rho \beta T a^3}{\mu^2}$$

$$\text{Prandtl Number} \dots N_{PR} = \frac{c_p \mu}{K}$$

$$\text{Rayleigh Modulus} = (N_{GR})(N_{PR})$$

I : INTRODUCTION

Increasing use is being made of liquid cooling media in many industrial processes involving the transference of heat. One of the properties required for the prediction of the heat transfer or the correlation of the results of such measurements is the thermal conductivity of the liquid. The convective heat transfer coefficients can be correlated in terms of dimensionless groups of the relevant physical properties which include the thermal conductivity. Therefore, accurate values of the thermal conductivity of liquids, are not only of prime importance in engineering applications, but are also necessary for the theoretical development of the physical sciences. It is a property that arises in all conduction and convective heat transfer problems and its importance in energy transport parallels that of viscosity in momentum transport.

The design and efficient operation of industrial heat transfer equipment employing liquids at high temperatures and pressures, demands reliable information concerning the physical properties of liquids and of these, thermal conductivity is particularly important. The available information on the thermal conductivity of liquids, however, is frequently uncertain. Data on the thermal conductivity of organic liquids are particularly scarce and almost non-existent at temperatures and pressures in use at present. Some values of this property for organic liquids of industrial importance are becoming available but they represent, for the most part, values determined at

relatively low temperatures and pressures.^{122,123*} Investigators have either held the temperature at a low selected value and subjected the liquid to increasing pressures or kept the liquid at a fixed pressure, usually atmospheric, and elevated the test temperatures. Almost all the available data for the thermal conductivity of organic liquid, therefore, is at atmospheric pressure and at temperatures below the boiling point of the liquid. Only one investigator, Abas-Zade,^{1,2(a)} has studied the combined effect of high pressures and temperatures on the thermal conductivity of organic liquids. He experimentally determined the thermal conductivity of Benzene, Toluene, and Xylene, at temperatures up to 752°F and pressures up to 200 atmospheres.

The operating temperatures and pressures are ever increasing for a number of reasons. The engineer and the scientist requiring more accurate thermal conductivity data for organic liquids for high temperature, or high temperature and high pressure applications, must extrapolate the existing low temperature values to the desired conditions. In many cases only one value exists and this must be used for all calculations. Such extrapolations are obviously questionable and, therefore, a need exists for the experimental determination of the thermal conductivity of organic liquids at high temperatures and pressures.

Certain high boiling organic substances such as biphenyl, phenyl ether, and their mixtures have long been used as heat transfer fluids because of their low vapor pressure and high resistance to pyro-

*Bibliography has been arranged in alphabetical order rather than the order of appearance.

lysis. Interest in these substances has recently been renewed, as they seem to offer advantages over other fluids as coolants and moderators in nuclear reactors, or even as working fluids in heat engines of nuclear power plants. The research described herein was undertaken for two main reasons. Firstly, to supply some of the missing data for the thermal conductivity of organic liquids being used or likely to be used in the atomic energy field. Secondly, to gain experience with standard methods for measurements up to 850°F and 150 PSI, in order to proceed with the development of other methods that may prove suitable for work at higher temperatures and pressures.

Up to now, almost all the known investigators have employed steady state heat conduction through a layer of liquid for the determination of the thermal conductivity. The basic equation describing pure conduction through a layer of substance is,

$$q = - K A \frac{\Delta T}{\Delta x}$$

where K is the thermal conductivity and the variables which must be accurately determined are: the liquid layer thickness (Δx), the temperature difference across the layer (ΔT) and the heat flow (q) through an area (A).

In all steady state measurements of the thermal conductivity, the heat transfer by convection and radiation across the layer in the cell must be avoided and the heat losses isolated for the measurements to have any meaning. For liquids, heat transfer by radiation is usually negligible but heat transfer by convection may be equal to or greater than the heat transfer by pure conduction. Elimination of

convection in various cell forms has been discussed in some detail in section IV of the thesis.

The use of a method depending on steady state heat conduction is time consuming due to the time required to establish thermal equilibrium. Rapid measurements can be obtained by employing transient heat conduction. The method is based on the transient temperature rise of a line heat source at a constant energy input. This method was first suggested by Schleiermacher¹²⁷ in 1888, but apparently no successful application was made of it until Van Der Held and Van Drunen,¹⁴⁹ in 1949, analysed the sources of error and developed a technique which removed the influence of heat capacity and density of the specimen from the determination. With transient methods, convective currents are avoided by making the measurements over a short period of time so that the density difference cannot develop the disturbing convection currents.

As a transport phenomenon many attempts have been made to derive the thermal conductivity of liquids from the purely theoretical grounds. The better known equations are given in the section dealing with the prediction of the thermal conductivity of liquids. The empirical correlations and the theoretical equations have been considered separately.

As an introduction to the cell designs, Fourier's heat conduction equation has been developed and applied to various geometrical configurations selected by the modern investigators. The cell forms that have been used by the researchers in determining the thermal con-

ductivity of liquids have briefly been summed up. The heat transfer in liquids by convection has been investigated and the importance of the $(N_{GR})(N_{PR})$ product in the cell designs pointed out.

Two apparatuses, the hot-wire cell and the concentric cylinder cell, were selected as suitable apparatuses; the first for its simplicity and the second for the higher pressure determinations. Both cells are described fully in this report.

The hot-wire cell is based on similar designs used by Goldschmidt⁵⁷ and Hutchinson⁶⁶, and employs the method of radial heat flow from a "hot" cylinder to a concentric "cold" cylinder. The liquid is contained in a small diameter Pyrex Brand glass tube with the heated filament in the center. The cell requires very small samples of the test liquids and reaches steady-state in a comparatively short period.

The concentric cylinder cell was designed such that the conducting liquid is contained in a 0.075 inch annular space, to minimize the possibility of convection. Heat, supplied by the heater located at the center of the inner cylinder, would be conducted radially from the inner to the outer cylinder. The temperature difference across the liquid layer is to be measured by six pairs of calibrated thermocouples and one pair of thermistors. Suitable guard heaters have been installed at each end of the cell, to compensate for any end losses and to provide a constant temperature zone for all leads. It was envisaged that this cell could be used for investigating various liquids over a wide temperature range, and that the convective currents would be absent at a temperature difference of 5°F or less across the liquid layer. The

cylindrical shape was chosen for convenient control of the heat losses as well as adaptability to a high pressure system.

A constant temperature bath was designed for operation of the thermal conductivity cells and complete details of the bath are given in the thesis. Two oils, a light transformer oil and a quenching oil having a high flash point, were employed to obtain the desired temperature range. The bath has been used for tests up to 600°F, but was designed for use up to 850°F, with a suitable bath medium, and a pressure of 150 PSI.

The bath temperature must be controlled closely for the thermal conductivity measurements to be sufficiently accurate. By using a mercury thermoregulator and continuously supplying the losses to the bath, temperature was controlled to $\pm 0.002^\circ\text{F}$ for about one hour periods. A thermistor-type temperature controller was designed for future work to control the bath temperature to at least $\pm 0.005^\circ\text{F}$ and it is described fully in this report.

The thesis also contains a complete description of the calibrations and the experimental procedure, the bath temperature control and all temperature measurements, and, the measurement of the power supplied to the test section while conducting the tests. Appendix I contains all the calibration data. Appendix II contains the accumulated experimental data and the available physical properties of the liquids tested. In Appendix III design details of the concentric cylinder cell, the thermistor-type temperature controller and the arc welding apparatus suitable for joining small diameter thermocouple conductors, are given.

The characteristics of the components employed in the construction of the thermistor-type temperature controller are outlined in Appendix IV.

The hot-wire cell was used to determine experimentally the absolute values of the thermal conductivity of Carbon Tetrachloride, Toluene, H.B.-40 and Hydrogenated Santowax OM. Carbon Tetrachloride and Toluene were investigated from about 70°F to near their respective boiling points, while H.B.-40 and Hydrogenated Santowax OM were tested from about 250°F to about 600°F. This work does not in any way represent a limit for the thermal conductivity measurements but serves to illustrate how values at higher temperatures can be determined. The experimental values for Carbon Tetrachloride and Toluene have been compared to the most reliable experimental values available in the literature. No direct comparisons could be made for HB-40 and Hydrogenated Santowax OM as no experimental data for these liquids were reported in the literature³ but comparisons with extrapolated data for similar organics have been made.

II : RELEVANT LITERATURE SURVEY

The first qualitative experiments on the thermal conductivity of liquids were reported by Rumford¹²¹ in 1786, whereas the first quantitative measurements of this property were performed by Despretz⁴¹ in 1838. However, it was not till 1923²³ that reliable experimental values of the thermal conductivity of liquids became available. The International Critical Tables⁶⁷ list what were considered to be highly reliable values of the thermal conductivity of sixteen liquids which were determined prior to 1923. In that year Bridgman²³ showed that the values for fifteen of these liquids were unreliable, with the result that the work prior to 1923 has now become of academic interest only and is of no particular value to the modern investigator.

Therefore only the work of the more important investigators since 1923 is considered relevant and a review of this work is presented in this section.

Experimental Work Subsequent to 1923

For the purposes of clarity and comparison, the methods of measurements were arbitrarily classified into the following two main groups and sub-groups.

GROUP I. - STEADY-STATE HEAT CONDUCTION

1. Thin Film Methods.
 - (a) Parallel Plate Cell : Film thickness varies between
0.00985 to 0.197 in.
 - (b) Concentric Cylinder Cell : Film thickness varies between
0.01 to 0.0156 in.
 - (c) Spherical Cell : Film thickness varies between 0.02 to
0.0395 in.
 - (d) Hot-Wire Cell : Film thickness varies between 0.0393 to
0.198 in.
2. Thick Film Methods.
 - (a) Parallel Plate Cell : Film thickness varies between
0.473 to 7.0 in.

GROUP II. - UNSTEADY-STATE HEAT CONDUCTION

1. Thin Film Methods.
 - (a) Hot-Wire Cell

For all the cases cited, the observer, the year that the work was carried out, the reference source, the film thickness employed, the film temperature drop, the temperature and the pressure range covered, the number and types of liquids investigated, are indi-

cated wherever such information is available.

Sakiadis and Coates, two notable contributors to the field of thermal conductivity of liquids, preceded their experimental determinations by tabulations of the existing information¹²².

The reliability scale adopted was as follows:

Excellent - $\pm 2\%$; Very Good - $\pm 5\%$; Good - $\pm 12\%$; Average - Reliable ; Poor - Unreliable.

The scale was based on considerations of the accuracy of determining the various factors entering the calculation of the thermal conductivity, and on whether the conditions of pure conduction were met in the apparatus. This scale has been adopted by the author for an attempt to assess the reliability of the work of other investigators. If the estimated experimental error of the results was greater than 12%, the work was considered unreliable.

GROUP I - STEADY STATE CONDUCTION

1 Thin Film Methods

(a) Parallel Plate Cell

Observer	Year	Ref.	Thick- ness inches	Film Temp. Drop OF	Tempera- ture Range Covered OF	Pressure Range Covered	Number and type of Liquids Investi- gated	Accuracy of Results
Kaye and Higgins	1927	75	0.00985 to 0.0197	Approx. 7.92		Atmos.	Nine Liquids	Average
Kaye and Higgins	1929	76	0.0134	5 to 9	234 to 410	Atmos.	Liquid Sulphur	Average
Martin and Lang	1933	90	0.0421		50 to 140.5	Atmos.	Water	Good
Erk and Keller	1936	45	0.118	12.6 to 21.6	42.8 to 161.5	Atmos.	Glycerol -water	Very Good
Riedel	1940	110	0.0394			Atmos.	Organic Liquids	Very Good
Fron- tasev	1946	52	0.197		70	Atmos.	Liquid- Liquid Solutions	Good
Riedel	1947	111	0.0394			Atmos.	Organic Liquids & mixture	Very Good
Kraus	1948	80	0.0157 0.0433 0.059	1.8 to 3.6	68 to 284 & 90 - 152.5	Atmos.	Glycols and Water	Good for Water

(a) (cont'd)

Observer	Year	Ref.	Thick- ness inches	Film Temp. Drop °F	Tempera- ture Range Covered °F	Pressure Range Covered	Number and type of Liquids Investi- gated	Accuracy of Results
Vargaf- tik	1950	151	0.197		69.8	Atmos.	Phenyl Hy- drazine - Acetal- dehyde	Good
Dick and McCready	1954	42	0.087 to 0.023	5.4 to 10.8	68 and 140	Atmos.	Nineteen Organic Liquid Compounds	Good
Sakiadis and Coates	1955	124	0.02		85 to 172	Atmos.	Fifty three Pure Or- ganic Liquids	Good
Chal- loner & Powell	1956	28	0.077 to 0.117	3.6 to 10.8	35.6 to 179.6	Atmos.	Seven Liquids	Very Good

(b) Concentric Cylinder Cell

Observer	Year	Ref.	Film Thickness inches	Film Temp. Drop °F	Temperature Range Covered °F	Pressure Range Covered	Number and type of Liquids Investigated	Accuracy of Results
Bridgman	1923	23	0.0156	1.08	86 and 167	1 to 11630 Atmos.	Fifteen Liquids	Average
Smith	1930	135	0.0156	1	86, 140, 167 and 212	Atmos.	Fifteen Liquids	Average
Dani-loff	1932	38	0.0156	1	86, 167 and 212	Atmos.	Seven Normal Primary Saturated alcohols	Average
Smith	1934	137	0.0156	1	86	Atmos.	Straight run and cracked gasoline	Average
Smith	1936	138	0.0156	1	86, 140 and 212	Atmos.	Twenty one Liquids	Average
Mark-wood and Benning	1943	89	0.0156	5 to 11	140, 167 and 320	Saturation Pressures	Six "Freon" Liquids	Average
Riedel	1948	112	0.01		68	Atmos.	Twenty five Hydrocarbons Thirty two Hydrocarbons Fifty six Compounds	Very Good
Riedel	1949	113	0.01		32 to 176	Atmos.	Sugar, solutions, fruit juices and milk	Very Good
Riedel	1950	115	0.01		Various	Atmos.	Mineral oils	Very Good
Riedel	1951	117	0.01		-112 to 176	Atmos.	Eighteen Organic Liquids	Very Good

(b) (Cont'd)

Observer	Year	Ref.	Film Thickness inches	Film Temp. Drop °F	Temperature Range Covered °F	Pressure Range Covered	Number and type of Liquids Investigated	Accuracy of Results
Riedel	1951	118	0.01			Atmos.	Mixtures of various organic liquids with water	Very Good
Uhlir	1952	147	0.01		Normal boiling to well above critical	Up to twice Critical	Liquid argon and Nitrogen	Very Good
Schmidt and Leidenfrost	1954	131	.0394 to 0.158		32 to 176	Atmos.	Toluene	Very Good
Pagerey St. Clair and Sibbit	1956	99	0.022	0.1 to 5	68 to 194	Atmos.	Ten organic Liquids	Very Good
Briggs	1957	24	.0276	3.6	68	Atmos.	Nineteen Organic Liquids	Good
Chal-loner and Powell	1958	29	.0492	3.6 to 9	68 to 149	Atmos.	Pyridine tri-fluoro tri-chloroethane, chlorofluoro-carbon oils	Very Good
Spencer and Todd	1959	139	0.04	7.74	-148 to -197		Liquid boron trifluoride	Very Good
Ziebland and Burton	1960	162	.00787	0.9 to 1.8	-167 to 500	Atmos.	Heavy water	Very Good
Scheffy and Johnson	1961	126	.0275	up to 7.2	154 to 529	Atmos.	eight Liquids	Very Good

(b) (Cont'd)

Observer	Year	Ref.	Film Thickness inches	Film Temp. Drop °F	Temperature Range Covered °F	Pressure Range Covered	Number and type of Liquids Investigated	Accuracy of Results
Ziebland and Burton	1961	163	.0102 and .0394	1.8	-4 to 233	Atmos.	Toluene	Very Good
Ziebland and Burton	1961	164	.0297	4.22 to 12.7	117 to 737	Atmos. to 4.62 Atmos.	Bi-phenyl Phenyl ether, Dow therm A Santowax R	Very Good
(c) <u>Spherical Cell</u>								
Riedel	1951	117	.0395		-112 to 176	Atmos.	Eighteen or ganic Liquids	Very Good
Richter and Sage	1957	109	0.020	2 to 4	40 to 100	14 to 340 Atmos.	Nitrogen dioxide in Liquid phase	Good
(d) <u>Hot-Wire Cell</u>								
Davis	1924	39	.0389		59 to 163.3	Atmos.	Toluene and Carbon tetra-chloride	Good
Kardos	1933	74			5 and 86	Atmos.	Toluene, ethyl and methyl chloride	Good
Timrot and Vargaf-tik	1940	145				1 to 400 Atmos.	Water	Very Good
Hutchinson	1945	66	0.195	1.8	64.4	Atmos.	Seven Liquids	Good
Abas-Zade	1947	1			up to 752	up to 200 Atmos.	Benzene and Toluene	Good

(d) (Cont'd)

Observer	Year	Ref.	Film Thickness inches	Film Temp. Drop °F	Temperature Range Covered °F	Pressure Range Covered	Number and type of Liquids Investigated	Accuracy of Results
Abas-Zade	1949	2			up to critical	up to critical	Benzene Toluene and Xylene	Good
Kern and Norstrand	1949	77	0.195	1.8	79.7 to 298.4	Atmos.	four fatty acids	Good
Cecil and Munch	1956	26	.0126	0.2 to .32	77	Atmos.	Five common liquids	Good
Cecil and Munch	1956	26	.0126	0.2 to .32	82 and 178	Atmos.	Sixteen mixtures of Aroclor 1248 & di(2 ethyl hexyl) adipate	Very Good
Cecil Koerner & Munch	1957	27	.0126	.02 to .32	86 to 423	Atmos.	Six pure Organic Liquids	Very Good

2. Thick Film Methods(a) Parallel Plate Cell

Observer	Year	Ref.	Film Thickness inches	Film Temp. Drop °F	Temperature Range Covered °F	Pressure Range Covered	Number and type of Liquids Investigated	Accuracy of Results
Kallan	1923	73		100		Atmos.	Water	Poor
Bates	1933	7	1.92	80	68 to 150	Atmos.	Distilled water and Red oil	Average
Louis and Carrette	1933	87				Atmos.	Oils	Average
Bates	1936	8	2	175		Atmos.	Liquid mixtures of glycerol and water	Good
Bates, Hazzard and Palmer	1938	9	2	122	50 to 158	Atmos.	Methyl alcohol-water & Ethyl alcohol water solutions	Good
Hamman	1938	62	0.473		-330	Atmos.	Liquid oxygen liquid nitrogen & their mixtures	Good
Bates, Hazzard & Palmer	1941	10	1	131		Atmos.	Twelve Chlorinated Hydrocarbons	Good
Bates and Hazzard	1945	11	1	160		Atmos.	Alcohols and Glycols	Good
Bates	1949	12	1	160		Atmos.	Liquid Silicones	Good

GROUP II - UNSTEADY-STATE HEAT CONDUCTION1. Thin Film Methods(a) Hot-Wire Cell

Observer	Year	Ref.	Temperature Range Covered °F	Pressure Range Covered	Number and type of liquids Investigated	Accuracy of Results
Van Der Held and Van Drunen	1949	149	57.2 to 76.7	Atmos.	Several Liquids and acid solutions	Very Good
Van Der Held, Hardebol and Kalshoven	1953	150		Atmos.	Water, Ethylene Glycol, Carbon tetra-chloride	Very Good
Allen	1958	4	72 to 176	Atmos.	Transformer oil	Good

III : EMPIRICAL CORRELATIONS AND THEORETICAL EQUATIONS FOR
THE PREDICTION OF THE THERMAL CONDUCTIVITY OF LIQUIDS

In practice, that is for an actual design, experimental data are necessary; for a conceptual engineering study experimental data may not be available and it is then necessary to resort to theoretical or semi-empirical expressions to obtain the required data. Theoretical considerations also assist in selecting the experimental techniques to be used and may uncover the weakness of a particular method. In addition they usually indicate suitable methods of expressing experimental data. A number of theoretical analyses are, therefore, reviewed in this section.

The basic relation for heat transfer by conduction originates from the French physicists Biot and Fourier⁵⁰. The formula, which is developed in the next section, states that the rate of heat flow by conduction in a material is equal to the product of the thermal conductivity of the material, the area of the section through which heat flows and the temperature gradient at the section. The thermal conductivity, therefore, is a physical property of the material and indicates the quantity of heat that will flow across a unit area if the temperature gradient is unity.

As a transport phenomena, many attempts have been made to derive thermal conductivity from purely theoretical considerations. Thermal conductivity can also be correlated with other properties of liquids such as the molecular weight, the viscosity, the velocity of sound in the liquid, the specific heat and the density. Many authors have tried to establish these correlations between the thermal conduc-

tivity of liquids.

In order to express the thermal conductivity by an empirical or a theoretical equation, an intimate knowledge of the internal structure of a liquid is necessary. In the past it was generally believed that because liquids flow and diffuse readily, their structure was similar to that of gases and the behavior of the molecules in liquids could be described by modifying the kinetic theory of gases. The physical model for the kinetic theory of gases is based on random molecular movement and one of the assumptions is that the molecules are of negligible size compared to mean free path of the movement. This theory yields the following equation.

$$K = \frac{1}{3} \rho \ell \bar{v}_m C_v \quad \dots \dots \dots \quad \text{..... (III.1)}$$

where 'K' is the thermal conductivity, ρ the density, ℓ the mean free path of movement, \bar{v}_m the mean molecular velocity and C_v the specific heat at constant volume.

On the other hand, more recently postulated theories assume that liquids are structurally closer to solids than gases. These theories are based on the fact that near the melting point the density of a liquid is close to that of a solid and, hence, there is little possibility of a free movement of the molecules within liquid. A brief description of the mechanism of heat transfer in solid follows without any emphasis being placed on mathematical derivations. Detailed mathematical treatments of the theory of heat conduction in solids and gases are given by Carslaw and Jaeger²⁵ and Jakob⁷⁰ in their respective text books.

When discussing heat transfer by conduction in solids, a clear distinction should be made between non-metallic and metallic substances. In non-metallic solids thermal conduction is only by lattice waves produced by atomic motions, while in metals and semi-conductors thermal conduction is considered to be by lattice waves and electrons.

The atomic motions in non-metallic solids assume the form of thermal vibrations which are regarded as a superposition of thermoelastic or thermo-acoustic waves known generally as lattice waves. Debye⁴⁰ was first to introduce the concept of lattice waves as a thermal-conducting medium in solids and the concept of thermal resistance due to scattering of the lattice waves by self-interference and lattice defects.

The thermal conductivity of semi-conductors is the effect produced by the transport of energy by the lattice waves and by electron movement. The wave concept can be used or the lattice wave can be considered as a "phonon-gas" and the electron movement as an "electron-gas". The potential causing the transport of energy by the phonon gas is the enthalpy gradient and resistance to flow the self-interference and lattice defects referred to above. This structural interference is almost independent of temperature but the self-interference increases with temperature. The "phonon-gas" concept leads to the following expression.

$$q = - \frac{\partial H}{\partial x} l c = - c_p l c \frac{dT}{dx} \quad \dots\dots\dots (III.2)$$

It is then apparent that:

$$K = \rho c_p l c \quad \dots\dots\dots (III.3)$$

Where

q = heat transferred per unit area in the "x" direction.

ℓ = the mean free path which consists of two parts; one for the self-interference and one for the defects.

C = the velocity of propagation of the "phonon-gas".

In the semi-conductor the concentration of electrons available to transport energy depends strongly on the temperature. In metals about 90 per cent of the thermal energy is transported by the electrons (except at very low temperatures) and thus a dependance between thermal conductivity and electrical conductivity exists. The expression defining this dependance is not revelant to the work that follows.

Based on the above discussed theories describing thermal conduction in liquids, many authors have proposed empirical and theoretical expressions to predict thermal conductivity. Weber¹⁵⁷ was first to propose such an expression in 1880 but since then other empirical and theoretical equations have been suggested and the more important ones, which are applicable to engineering calculations, are listed in this section.

Section A : Empirical Correlations

(1) WEBER'S EQUATION

One of the earliest expressions relating thermal conductivity to other properties of liquids is that proposed by Weber¹⁵⁷. He first gave his expression as $\frac{K}{\rho C_p} = \text{constant}$, but later modified it to:

$$K = 0.00359 C_p \rho (\rho/M)^{1/3} \dots\dots\dots (III.4)$$

Where

K = thermal conductivity, Cals/(Sec)(Cm)(°C)

0.00359 = Constant, Cm³/Sec

C_p = Specific heat, Cals/(Gm)(°C)

ρ = density of liquid, Gms/(Cm)³

M = Molecular weight, Gms

It will be noted that (ρ/M) is the mole volume and $(\rho/M)^{1/3}$ has the dimension of a length and the equation is thus analogous to the expression describing the "phonon-gas" concept.

Smith^{137,138} compared values calculated by using equation (III.4) with the observed experimental results and found that better agreement could be obtained by changing the constant of the equation. This resulted in Weber's modified equation which is,

$$K = 0.0043 C_p \rho (\rho/M)^{1/3} \dots\dots\dots (III.5)$$

Dick and McCready⁴², in their investigation of the thermal conductivity of some organic liquids found that the values obtained by using equation(III.5) were about 25 per cent lower than their experimental results.

(2) SMITH'S EQUATIONS

Starting in 1930, Smith¹³⁵ proposed a series of entirely empirical correlations for calculating the thermal conductivity of liquids. The first equation of the series is that,

$$K = 8.1 \times 10^{-4} \frac{\rho^{2.15} C_p^{1.55} M^{0.192}}{\mu^{0.12}} \dots\dots\dots (III.6)$$

Where

K = thermal conductivity, Cals/(Sec)(Cm)(°C)

ρ = density of liquid, Gms/(Cm)³

C_p = specific heat, Cals/(Gm)(°C)

M = Molecular weight, Gms

μ = viscosity, Centipoises

Smith¹³⁵ found that equation(III.6) satisfied the fifteen liquids for which experimental data was available at the time. The agreement with experimental values was within 4.5 per cent for all liquids except two oils. In the original paper¹³⁵, the errors for these oils were quoted as about 6 and 9 per cent but were modified to 3 and 20 per cent respectively in a subsequent paper¹³⁸. He tested equation (III.6) with additional experimental data obtained in 1936 and found that the agreement with the new data was poor.

Dick and McCready⁴² also compared their experimental values with those obtained with equation (III.6) and found that the calculated values were consistently higher.

In 1936, Smith¹³⁸ could see little chance of modifying the exponents of equation (III.6) to satisfy all liquids, so he tried a different approach. By taking variations from approximate mean values he found that,

$$K_{\text{at } 30^{\circ}\text{C}} = 0.000361 + \frac{(C_p - 0.45)^3}{155} + \frac{(\rho/M)^{1/3} - 0.20}{800} + \frac{\mu^{1/9} - 1}{10,000} \dots \dots \dots \text{(III.7)}$$

This is equivalent to

$$K_{\text{at } 30^{\circ}\text{C}} = 0.000011 + \frac{(c_p - 0.45)^3}{155} + \frac{(\rho/M)^{1/3}}{800} + \frac{\nu^{1/9}}{10,000}$$

..... (III.8)

The units of equations (III.7) and (III.8) are the same as in equation (III.6) except that ν is kinematic viscosity in centistokes.

Smith¹³⁸ compared his experimental results with the values obtained from equation (III.8) and found the average error to be about 6.7 per cent. Based on this comparison, Smith considered equation (III.8) to be satisfactory for engineering use.

(3) CRAGOE'S EQUATION

In 1929, Cragoe³⁵ proposed the following equation to facilitate calculations of the thermal conductivity of petroleum liquids. He stated that,

$$K = \frac{0.813}{d} [1 - 0.0003 (t - 32)]$$

..... (III.9)

Where K = thermal conductivity, Btu/(Hr)(Ft)²(°F/in.)

d = specific gravity at 60°F

t = temperature, °F

Smith¹³⁸ compared the values obtained by employing equation (III.9) with those observed experimentally and found that the average error was 12.7 per cent, with a maximum error of 39 per cent. When he assumed a constant value of 0.000327 Cals/(Sec)(Cm)(°C) for the thermal conductivity of oils at 30°C, the average error was 6 per cent and the maximum error was plus or minus 13 per cent.

Cragoe's equation was also tested by Dick and McCready⁴². The comparison of calculated values with the experimental results gave a maximum error of 21 per cent, which was slightly better than what Smith found for the oils he used. When Dick and McCready used the constant value 0.000327 recommended by Smith, the maximum error was reduced to 19 per cent.

(4) PALMER'S EQUATION

While checking values of thermal conductivity of liquids obtained by using Weber's equation (III.4), Palmer¹⁰⁰, in 1948, modified this equation by introducing in it the Trouton's constant and the molal entropy of vaporization. Palmer suggested that,

$$K = A \rho C_p (\rho/M)^{1/3} \cdot \frac{L_b/T_b}{L_{vap}/T_B} \dots\dots\dots (III.10)$$

Where:

K = thermal conductivity, Cals/(Sec)(Cm)(°C)

A = Constant, Cm³/Sec

ρ = density, Gms/Cm³

C_p = specific heat, Cals/(Gm)(°C)

M = molecular weight, Gms

L_b/T_b = Trouton's Constant, Cals/(Mol)(°K)

L_{vap}/T_B = Molal entropy of vaporization, Cals/(Mol)(°K)

Trouton's constant is defined by Trouton's rule which states that the molecular heat of vaporization of normal liquids at the boiling point under atmospheric pressure divided by the absolute

boiling temperature is a constant and is approximately equal to 21.

Palmer found that if $21 \times A$ was taken as 0.0947, the magnitude of error between experimental values and those obtained by using equation (III.10) was reduced.

(5) RIEDEL'S EQUATION

In 1951, Riedel¹¹⁷ worked out the following equation relating thermal conductivity of liquids to reduced temperature.

$$\frac{K}{K_{\text{crit}}} = 1 + 6.7 \left(1 - \frac{T}{T_{\text{crit}}}\right)^{2/3} \quad \dots\dots\dots \text{(III.11)}$$

In the above equation K_{crit} is an empirical parameter which has the formal significance of the thermal conductivity coefficient at the critical temperature¹¹⁶, T_{crit} is the critical temperature and $\frac{T}{T_{\text{crit}}} = T_r$, the reduced temperature. This approach essentially assumes that the thermal conductivity follows the law of corresponding states. If K_{crit} is unknown, two determinations of the thermal conductivity at different temperatures are necessary to allow the use of equation (III.11)

Section B : Theoretical Equations

The theory of the liquid state of substances has not been developed to the point where a satisfactory equation for thermal conductivity may be arrived at without vitiating assumptions. A simplified theoretical equation is therefore desirable; one such equation was developed by Bridgman²³ and the equation is surprisingly successful in spite of its simplicity.

Since Bridgman proposed his equation other theoretical equations have been proposed and more important of these are given in this section.

(1) BRIDGMAN'S EQUATION

In 1923, Bridgman²³ derived an expression for the thermal conductivity of liquids which implied a relationship between the thermal conductivity and the velocity of sound in a respective liquid. Bridgman's equation states that,

$$K = \frac{2RU}{d^2} \text{ Cals}/(\text{Sec})(\text{Cm})(^\circ\text{C}) \quad \dots\dots\dots (\text{III.12})$$

Where K is the thermal conductivity, R is the universal gas constant in heat units, U is the velocity of sound in the liquid, and d is the mean distance between the centers of molecules and is equal to $(M/\rho)^{1/3}$.

Bridgman²³ tested values obtained by employing equation (III.12) with those he determined experimentally for eleven liquids. The comparison showed that the average error between the calculated and the observed thermal conductivities was 16.6 per cent, with a maximum error of 38 per cent.

Smith¹³⁸ determined experimental thermal conductivity values of several other liquids for which the velocity of sound was available. A check between these experimental values and those obtained from equation (III.12) gave an average error of 15.2 per cent and the maximum error of 39 per cent.

Dick and McCready⁴² found that the values of thermal conductivity obtained from Bridgman's equation were consistently higher than

their experimental results for high molecular weight organic liquids.

Sakiadis and Coates¹²⁴ obtained experimental values of the thermal conductivity of twenty eight liquids and compared them to those determined by using equation (III.12). The comparison showed that the average deviation of the calculated from the observed values was ± 15 per cent, while the maximum deviation was ± 40 per cent.

(2) RAO'S EQUATION

Rao¹⁰⁷ again reverted to a molecular theory of solids whereby the atoms are considered to be simple-harmonic oscillators and proposed the following equation.

$$K = 2.096 \times 10^5 \left[\frac{T_s}{M V_s^{4/3}} \right]^{\frac{1}{2}} \text{ Cals/ (Sec)(Cm)(}^\circ\text{C)} \dots \text{ (III.13)}$$

Where K = thermal conductivity,
 T_s = melting temperature ($^\circ\text{C}$)
 M = molecular weight (Gms)
 V_s = molecular volume (Cm^3)

Dick and McCready⁴² extrapolated their experimental thermal conductivity values for the high molecular weight compounds investigated from 20°C to the freezing point. A comparison between these extrapolated values and those obtained from equation (III.13) showed the calculated results to be consistently higher than the observed values by a factor of about 2.

(3) FOURNIER'S EQUATION

Fournier⁵¹ derived an equation for calculating the thermal conductivity of liquids. His discussion was based on the cage theory

of liquids suggested by Polissar¹⁰³. In deriving his equation, Fournier assumed that the molecules of the liquid in their cages undergo motions intermediate between the harmonic motion of crystalline solids and the translational motion of gases. Fournier's equation states that

$$K = \frac{C_v^2 L^2 T}{V^2 \mu} \text{ Cals/((Sec)(Cm)(}^\circ\text{C))} \quad \dots\dots\dots \text{(III.14)}$$

where K is the thermal conductivity, C_v is the molar heat capacity at constant volume, L is the mean distance between molecules, T is the absolute temperature, V is the molar volume, and μ is the coefficient of viscosity.

Tyrrell¹⁴⁶ states that equation (III.14) is moderately successful for roughly spherical molecules but gives values which are much too small for chain molecules such as hexane.

(4) SAKIADIS AND COATES' EQUATION

Sakiadis and Coates¹²⁴, in 1955, derived an equation for predicting the thermal conductivity and its temperature coefficient of pure organic liquids. The equation was based on a particular molecular arrangement in the liquid, consistent with the results of X-ray diffraction studies in liquids. The theoretical equation of Sakiadis and Coates states that,

$$K = C_p U \rho L \text{ Btu/(Hr)(Ft)(}^\circ\text{F)} \quad \dots\dots\dots \text{(III.15)}$$

where

C_p = specific heat at constant pressure, Btu/(Lb)($^\circ$ F)

U = velocity of sound in the liquid, Ft/Hr

ρ = liquid density, Lb/Ft³

L = available intermolecular distance, Ft.

Sakiadis and Coates¹²⁴ compared the values obtained from equation (III.15) with the experimental values they obtained for forty-two liquids. The comparison showed that the average deviation of the calculated from the observed values was ± 2.6 per cent, while the maximum deviation was about ± 6 per cent.

IV : INTRODUCTORY HEAT TRANSFER THEORY AS APPLIED
TO THE THERMAL CONDUCTIVITY CELL DESIGN

By applying a temperature gradient across a liquid layer, heat can be transferred from the region of higher temperatures to that of lower temperatures by one or more of the following modes.

- (a) Conduction, which is a process by which thermal energy is transmitted by direct molecular communication.
- (b) Convection, which is by mass motion of energy-containing fluid particles from the hot to the cold zone.
- (c) Radiation, which is transport of thermal energy in the form of electromagnetic waves and consequent absorption of radiant energy.

In any thermal conductivity measuring apparatus, the heat transfer by convection and radiation should be eliminated. The equations governing heat transfer by conduction in various possible geometrical configurations are derived and then the elimination of heat transfer by convection and radiation is discussed briefly.

The fundamental relation for the conduction of heat in fluids (liquids and gases) is the same as for solids. The steady flow of heat by pure conduction was studied by the French physicists Biot and Fourier⁵⁰ and may be expressed by:

$$Q_x = \frac{dQ}{dt} = - KA \frac{\Delta_x T}{\Delta X} \quad \dots\dots\dots (IV.1)$$

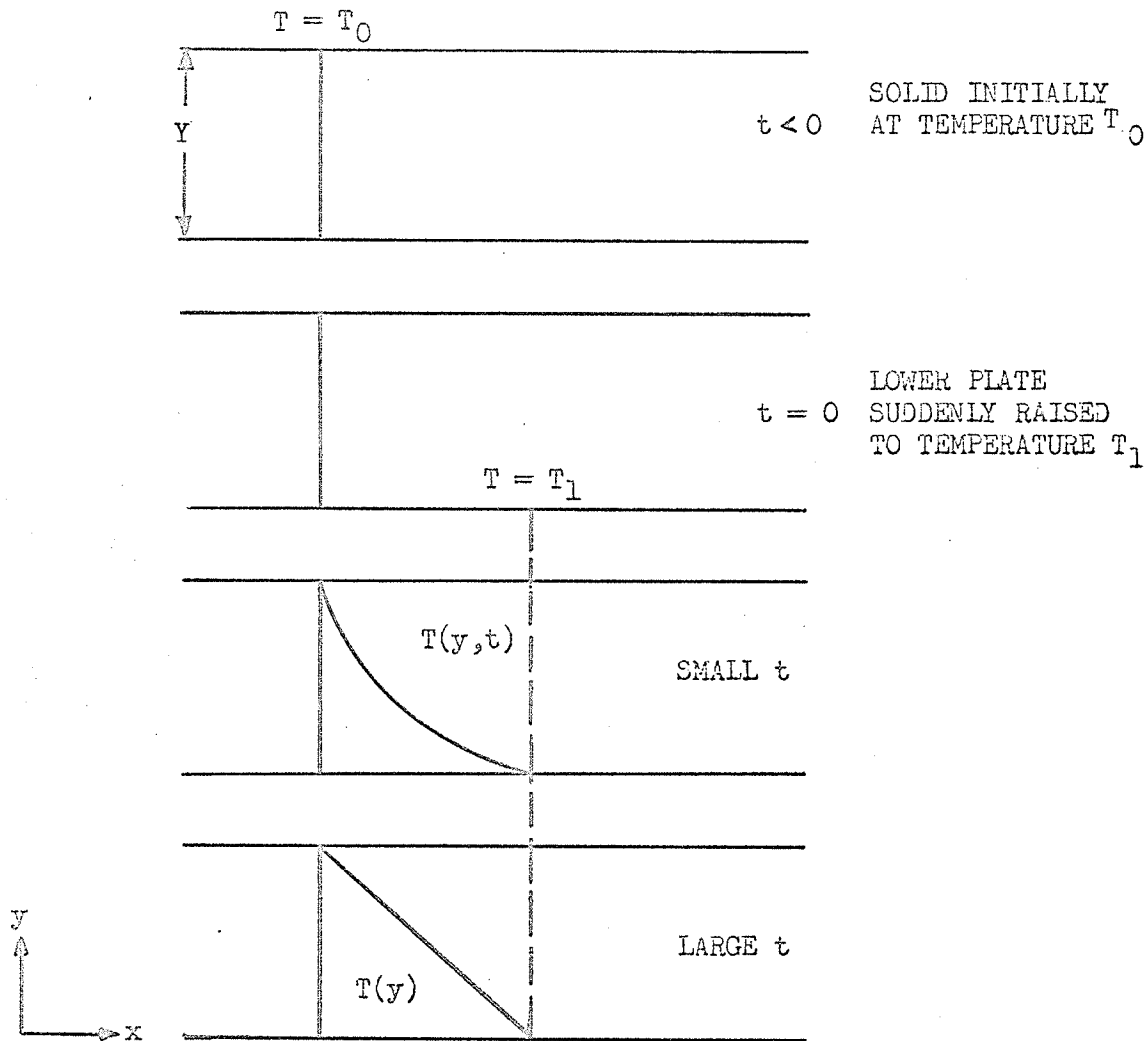
This formula implies the assumption of a homogeneous substance in which a constant temperature difference $\Delta_x T$ is held between the points of a plane area A and any points at a short perpendicular distance ΔX from this area. Then, a steady rate of heat flow q_x , per unit time, occurs in the direction of the decreasing temperature. The factor of proportionality 'K' is called "heat conductivity" or thermal conductivity.

1. Development of Fourier's Law of Heat Conduction

Consider a slab of solid material of area A between two large parallel plates a distance Y apart. Initially (for time $t < 0$) the solid material is at a temperature T_0 throughout. At time $t = 0$, the lower plate is suddenly brought to a slightly higher temperature T_1 and maintained at that temperature. As time proceeds, the temperature profile in the slab changes, and ultimately a linear steady-state temperature distribution is attained, as shown in the diagram on the following page.

During the transient period the relationship between temperature (T), time (t), and position y is governed by the following differential equation and the appropriate boundary conditions.

$$\frac{\partial T}{\partial t} = \frac{K}{\rho C_p} \frac{\partial^2 T}{\partial y^2} \quad \dots\dots\dots (IV.2)$$



DEVELOPMENT OF FOURIER'S LAW OF HEAT CONDUCTION

Fig (a)

When the steady state has been reached, the heat flow per unit area across a given plane becomes the same at all planes in the solid layer, the temperature distribution is invariant with time, and it is possible to write Fourier's law in the form:

$$q_y = -K A \frac{\Delta T}{\Delta y} \dots\dots\dots (IV.3)$$

Most measurements of thermal conductivities of liquids have been made by employing equation (IV.3). If q , the rate at which heat is transferred by pure conduction across the liquid layer and the temperature gradient $\frac{\Delta T}{\Delta y}$ are measured when the steady state is attained, the thermal conductivity can be calculated from this equation. In theory the procedure for the experimental determination of thermal conductivity of liquids looks simple but some of the major experimental difficulties are the time required for each determination, the prevention of heat losses due to end effects, and an accurate determination of the heat transferred across the liquid layer. For the experimental determination of the thermal conductivity of solids, the quantity $\frac{K}{\rho c_p}$ can be obtained from a suitable integrated form of equation (IV.2) by measuring the temperature in the sample as a function of position and of time during the period prior to the establishment of the steady state. This method was applied to liquids by Soonalawa¹⁴⁰ but the results were not encouraging¹⁴⁶. Most widely used^{46,55,56,149,150} non-steady state methods for measuring the thermal conductivity of liquids are based on a measurement of the rate at which heat is lost from a thin metallic filament immersed in the test liquid.

Equation (IV.3) is the one-dimensional form of Fourier's law of heat conduction, valid when T is a function of y . It states that the heat flow by conduction is proportional to the temperature gradient.

In an isotropic medium in which the temperature varies in all three directions, an equation like (IV.3) can be written for each of the co-ordinate directions.

$$q_x = -KA \frac{\partial T}{\partial x} \dots\dots\dots (IV.4)$$

$$q_y = -KA \frac{\partial T}{\partial y} \dots\dots\dots (IV.5)$$

$$q_z = -KA \frac{\partial T}{\partial z} \dots\dots\dots (IV.6)$$

By an isotropic medium it is meant that the coefficient K in equations (IV.4), (IV.5) and (IV.6) has the same value in all three directions. The assumption of isotropy is satisfactory for fluids and for most homogeneous solids; the principal non-isotropic materials are single non-cubic crystals and fibrous or laminated solids.

The above relations are the components of the single vector equation:

$$q = -KA \nabla T \dots\dots\dots (IV.7)$$

which is the three-dimensional form of Fourier's law. It states that the heat flow vector q is proportional to the temperature gradient ∇T and is opposite in direction.

Of all the various types of apparatuses used by investigators, the more important of these have been characterized by the steady-state heat conduction across a thin layer of the test liquid. Various types of mechanical designs have been used. The test liquid has been enclosed between two parallel flat plates or two concentric cylinders. Riedel¹¹⁷⁻¹¹⁹ and Richter and Sage¹⁰⁹ seem to be the only investigators who have successfully adopted the concentric-sphere cell for the thermal conductivity measurements of liquids. The basic relationships for the steady state heat transfer by conduction through the above mentioned geometrical arrangements are developed.

(a) Steady-State Heat Flow Through A Plane Wall

For the simple case of steady-state heat flow through a plane wall, the temperature gradient and the heat flow do not vary with time and the cross-sectional area along the heat flow path is uniform. The basic Fourier's equation (IV.1) has already been stated for a plane area. If the plane wall has a finite length "L", then the variables in equation (IV.1) can be separated and integrated between the appropriate limits to yield the following equation.

$$q = \frac{KA}{L} (T_{\text{hot}} - T_{\text{cold}}) \quad \dots\dots\dots (IV.8)$$

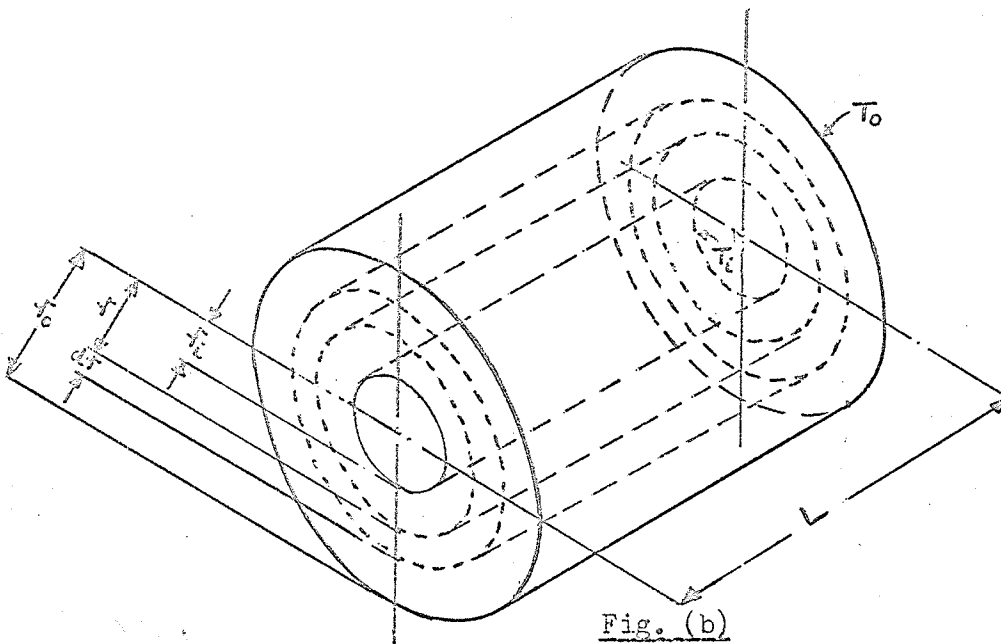
(b) Steady-State Heat Flow Through A Hollow Cylinder

Fig. (b)

Equation (IV.1) may be rewritten in the following manner,

$$q = -K A \frac{dT}{dr} \quad \dots\dots\dots (IV.9)$$

based on the assumption that the temperature at any point in the hollow cylinder can be expressed as a function of the radius only. Thus isotherms, or lines of constant temperature, are concentric circles lying between the inner and outer cylinder boundaries.

If the cylinder is homogeneous and sufficiently long that end effects may be neglected and the inner surface temperature is maintained constant at T_i while the outer surface temperature is maintained uniformly at T_o , the rate of heat conduction is as in equation (IV.9) where $\frac{dT}{dr}$ is the temperature gradient in the radial direction. For a cylinder of finite length "L", the variables in equation (IV.9) can be separated and then integrated between the appropriate limits to yield the following equation.

$$q = \frac{2\pi LK (T_i - T_o)}{\ln \frac{r_o}{r_i}} \dots\dots\dots (IV.10)$$

(c) Steady-State Heat Flow Through a Spherical Shell

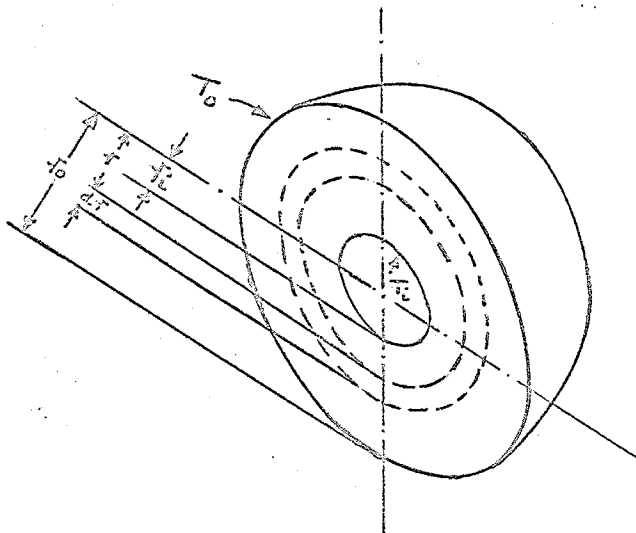


Fig. (c)

Conduction through a spherical shell is also a one-dimensional steady-state problem if the interior and exterior surface temperatures are uniform and constant. Equation(IV.9) can be written in the following form:

$$q = -K (4\pi r^2) \frac{dT}{dr} \dots\dots\dots (IV.11)$$

The variables in the above equation can be separated and then integrated between the appropriate limits to yield the following equation:

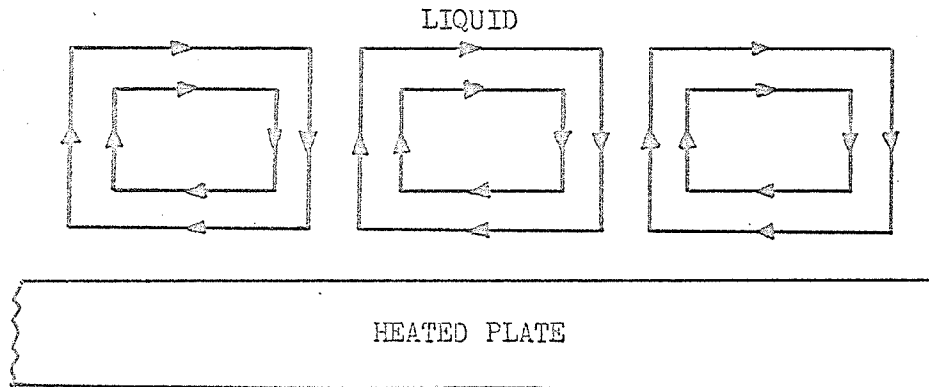
$$q = \frac{4\pi r_i r_o K (T_o - T_i)}{r_o - r_i} \dots\dots\dots (IV.12)$$

As already mentioned the heat transfer by convection and radiation in a thermal conductivity cell must be avoided. In most thermal conductivity measurements for liquids, small temperature differences are employed between the 'hot' and 'cold' cylinders. Also most liquids are opaque to infra-red radiation and, consequently, heat transfer by radiation in liquids can be ignored.

Heat transfer by natural convection in a thermal conductivity cell will be significant unless precautions are taken to avoid convection. In a cell where the liquid is enclosed between two horizontal plates, the natural convection currents in the liquid will be kept to a minimum if the heat flows from the upper to the lower plate.

In a parallel-plate cell where the lower plate is hotter than the upper plate, convection currents will not commence until the product of Grashof number (based on distance and temperature difference

between the plates) and Prandtl number (Rayleigh Modulus) reaches about 1700^{44} . When this value of the product of Grashof and Prandtl numbers is reached 'Cellular motion', first studied experimentally by Bénard in 1900, develops in the liquid. This flow pattern is shown in the following diagram.¹⁴⁶ The liquid in the interior of these cells moves



DEVELOPMENT OF 'CELLULAR MOTION' ON A FLAT PLATE

Fig. (d)

in an upward direction and returns downward near the boundaries of the neighboring cell. The 'cellular motion' remains unchanged till a value of the product of Grashof and Prandtl numbers of about 47,000 is reached when it changes to irregular turbulence⁴⁴. Rayleigh¹⁰⁸, in 1916, theoretically calculated the lower critical Reynolds number at which 'cellular motion' commences and, consequently, the product of Grashof and Prandtl numbers is called Rayleigh's Modulus.

When the liquid layer is contained between two horizontal concentric cylinders, 'cellular motion' or convective currents do not commence if the value of Rayleigh's modulus is below 1000 and this value of Rayleigh's modulus can also be taken as a limit for the

apparatus where the liquid is contained between two vertical concentric cylinders¹⁴⁶. Eckert⁴⁴ states that in a thermal conductivity measuring apparatus where the liquid is contained between two vertical walls, the heat transfer takes place by pure conduction if,

$$N_{Gr} < 124 (N_{Pr})^{-2} \left(\frac{20}{21} + N_{Pr} \right) (L/b) \quad \dots\dots\dots (IV.13)$$

where:

- N_{Gr} = Grashof number
- N_{Pr} = Prandtl number
- L = Layer height
- b = Layer thickness

He further states that near the lower and upper ends of the walls the temperature drop across the layer is non-linear over a height at each end equal to the layer thickness. This situation can be avoided by providing guard heaters at each end and by making the height of the walls considerably greater than the liquid layer thickness.

2. Cell Forms Employed By Other Investigators

The forms of cells, based on the geometrical configurations already discussed, which have been employed by other investigators can be briefly summed up as follows:

(a) A Disc Type Cell

A disc type cell consists of a thin layer of liquid between 0.01 inch to 0.20 inch thick, enclosed between two parallel plates. The upper plate is usually the heated plate while the bottom plate is cooled.



Heating is accomplished either electrically or by circulating hot water over the top plate. Thermocouples are employed for temperature measurements.

(b) A Concentric Cylinder Cell

The concentric cylinder apparatus utilizes the annular space to enclose the test liquid. Heat is supplied by a resistance heater at the center of the inside cylinder, usually called the emitter. The apparatus is usually enclosed in a steel cylinder and immersed in a constant temperature bath. Temperature measurements are usually made with thermocouples. The liquid film thickness varies from approximately 0.015 inch to 0.100 inch. The rugged construction of this apparatus makes it readily adaptable for high pressure measurements.

(c) A Hot-Wire Cell

Another thermal conductivity cell which may be considered a modification of the concentric cylinder apparatus is the hot-wire type cell. It consists essentially of a wire affixed co-axially in a cylindrical tube, of either pyrex or a metal. The cell is placed in a constant temperature bath. The filament or the wire used is usually platinum or tungsten and heating is accomplished by applying a voltage to the wire and the wire serves both as a heater and a resistance thermometer. The film thickness is usually between 0.04 inch to 0.20 inch.

(d) A Concentric Sphere Cell

Riedel¹¹⁶⁻¹¹⁸ & Richter & Sage¹⁰⁹ seem to be the only investigators who employed a sphere for the thermal conductivity measurements of liquids. Riedel's cell was a copper sphere enclosed in a copper block giving an all round clearance of 0.0395 inches. Platinum resistance thermometers were used to measure the temperature close to the liquid metal interface.

(e) Other Cell Forms

Some of the less important apparatuses are the thick film and the unsteady-state designs. The thick film method utilizes a relatively large film thickness which varies from 0.473 inch to 7 inches. This method requires a large temperature drop across the liquid layer and in some methods reaches 175°F. The accuracy of these apparatuses are dependant upon careful thermal guarding and to insure no heat losses. Corrections for heat transfer by radiation and convection across the liquid layer are also necessary for reliable thermal conductivity values. In many cases these requirements were not met by the investigators using these apparatuses.

Unsteady-state methods have been used by some recent investigators. These methods are characterized by discontinuous heat transfer across the liquid layer. The thermal conductivity is calculated by assuming certain boundary conditions and integrating the differential equation of Fourier.

Experimental determinations of the thermal conductivity of fluids can be made with the aid of relative or absolute methods.¹⁶³ Common

pre-requisites for all absolute determinations are the accurate knowledge of certain characteristic dimensions of the conductivity cell and the absence of noteworthy heat losses or gains from or to the cell. The factors to be considered are, therefore:

- (a) Accuracy of measurement of the physical dimensions of the apparatus.
- (b) Accuracy of measurements of temperatures and temperature drops.
- (c) Accuracy of measurement of heat flow.
- (d) Heat losses by convection and radiation and corrections to be made.
- (e) Reproducibility of results.

High precision is required in the fabrication and in the assembly of conductivity cells for absolute determinations and in many instances the resulting high cost of the equipment cannot be justified for determinations of a routine character requiring less accuracy. Hence apparatuses of a simpler design and greater ease and higher speed of operation have often been used in the past in which determination were made relative to another fluid with an established thermal conductivity. The accuracy of such measurements depends therefore in the first place on the reliability of the values of the calibration fluid.

With the exception of several substances whose thermal conductivity has been well established in the gaseous state, there is, liquid water excluded, no other substance whose thermal conductivity is sufficiently accurately known over a wide range of temperature in order to recommend it as a calibration or a control fluid. A study of the rele-

vant literature shows that discrepancies of up to 30% between different workers' values for a certain substance are by no means a rarity.

For purely scientific purposes the Joule is used as the energy unit since the heat flow in steady state processes is usually measured electrically, length is measured in centimeters, time in seconds and temperature in degrees centigrade. This gives the units of thermal conductivity as Joules - $\text{Cm}/(\text{Sec})(\text{Cm})^2(^{\circ}\text{C})$.

In engineering, the British Thermal Unit is used as the energy unit, the length is measured in feet, time in hours, and temperature in degrees Fahrenheit. This leads to the units of thermal conductivity as $\text{Btu-Ft}/(\text{Hr})(\text{Ft}^2)(^{\circ}\text{F})$ or $\text{Btu}/(\text{Hr})(\text{Ft})(^{\circ}\text{F})$.

V : DESIGN OF EQUIPMENT

As this work marks the beginning of the programme on an investigation of methods suitable for the absolute measurements of the thermal conductivity of liquids, all the necessary equipment had first to be designed and built before any tests could be performed. In all, two cells suitable for the thermal conductivity measurements, a constant temperature oil bath, an on-off type and a thermistor-type temperature controllers, and a device suitable for welding small diameter thermocouple wires, were designed. The design details of the equipment actually employed for the investigations reported in the thesis are outlined in this section while the details of the remaining equipment are given in Appendix III. The designs of the hot-wire cell, the constant temperature oil bath and the on-off type temperature controller are described in this part. Appendix III contains complete design details of the concentric cylinder cell, the thermistor-type temperature controller and the device suitable for welding small diameter thermocouple wires.

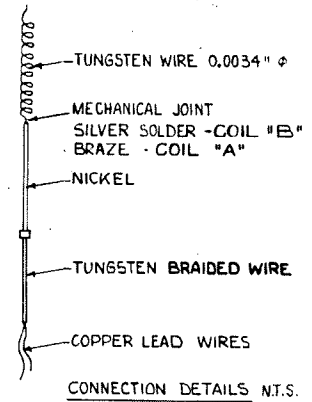
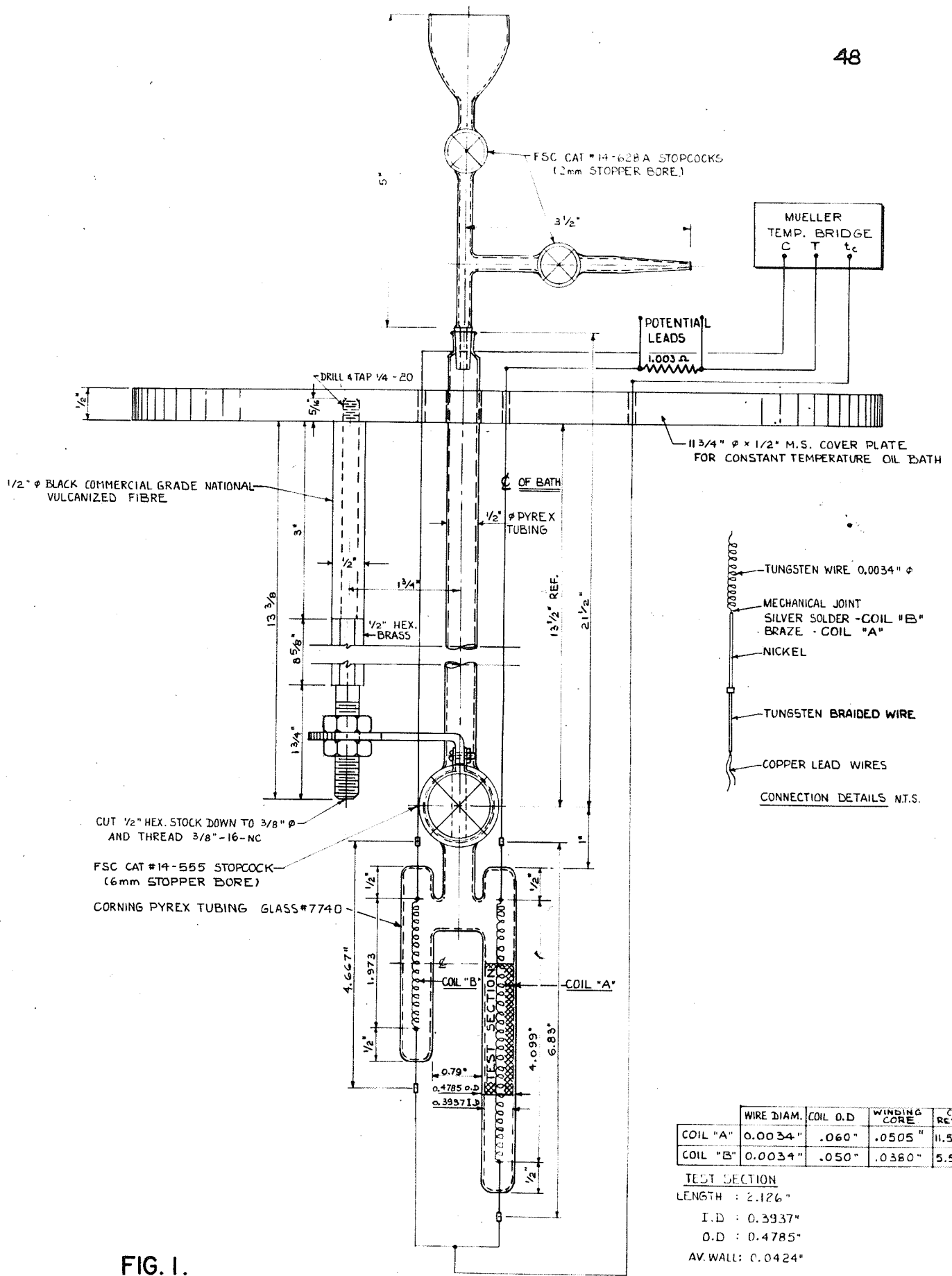
1. The Hot-Wire Cell

In any cell to be employed for the steady state measurements of the thermal conductivity of liquids, heat transfer by convection should be eliminated. The liquid layer should not be made so thick that large temperature differences are necessary to transfer heat, neither should the layer be made so thin that its thickness cannot be measured accurately. A bulky and an unnecessarily large cell should be avoided in order to

eliminate long periods of time that may be required by the cell to attain steady state. One type of cell which meets these requirements is a hot-wire cell which in fact is a modification of the concentric cylinder type.

The hot-wire technique was first used by Goldschmidt⁵⁷ and more recently revised by Hutchinson⁶⁶, Cecil and Munch^{26,27} and Waterman¹⁵⁶. Hutchinson utilized a single tube, with no compensation for end losses, containing a coiled hot-wire filament. This fact, in conjunction with the lack of correction for end effects made absolute measurements impossible and it was necessary for Hutchinson to calibrate the cell against known standards. Discrepancies and uncertainties existing in the literature, however, make the choice of suitable calibration liquids difficult.

A highly refined modification of the hot-wire method has been used in this research. A hot-wire cell, shown in Fig. 1, was designed to eliminate end effects which existed in Hutchinson's apparatus⁶⁶. The cell is a modification of Hutchinson's apparatus and incorporates the method used by Goldschmidt⁵⁷, and, consists of two units identical in all respects except length. One half of coil B simulates an equivalent length in the upper part of Coil A, while the other half of coil B simulates an equivalent length in the lower part of coil A. Thus power consumption and losses in the end sections are identical if the same current is passed through both units. The end losses from the test section can, therefore, be compensated for electrically, and the power and resistance of the test section obtained easily. The coiled filaments are made from 0.0034 inch diameter tungsten wire, and accurately centered in the



	WIRE DIAM.	COIL O.D.	WINDING CORE	COLD RESISTANCE
COIL "A"	0.0034"	.060"	.0505"	11.505 Ω
COIL "B"	0.0034"	.050"	.0380"	5.536 Ω

TEST SECTION
 LENGTH : 2.126"
 I.D : 0.3937"
 O.D : 0.4785"
 AV. WALL: 0.0424"

FIG. I.

REMARKS THERMAL CONDUCTIVITY OF LIQUIDS	UNIVERSITY OF MANITOBA DEPARTMENT OF MECHANICAL ENGINEERING			
	DRAWN	H.W.	SCALE:	SHEET
	DATE	FEBR 21 1963	FULL SIZE	NB
APPROVED			NO. OF SHEETS	5
HOT WIRE APPARATUS			DRAWING NO.	H2 - 7

glass tubes.

The filling tube protrudes through the central circular bath cover a distance of about 6.5 inches. At this point a special removable connector is attached to the filling tube. This connector consists basically of a filling cup and a pressure attachment which enables the liquid in the cell to be pressurized, if so desired. The hot-wire cell, with the centre line of the test section in line with the vertical centre line of the constant temperature bath, is held in place by a special clamp. This special clamp is attached to a vertical, threaded, hexagonal brass bar 13 3/8 inches long which is screwed into the underside of the bath cover.

The cell was tested under high vacuum to find any leaks but none were located. The glass work in the manufacturing of the cell was carried out by the Chemistry Department, University of Manitoba.

If properly used, this cell is capable of providing accurate data and since the temperature of the surrounding bath determines the maximum operating temperature, the equipment can easily be used to determine the thermal conductivity of any liquid within a temperature range of -300 to 1000°F , as long as the liquid is compatible with glass and tungsten.

The cell is inexpensive and relatively easy to manufacture. It uses small quantities of test liquids and can be used for liquids which would normally attack metals.

2. The Concentric Cylinder Cell

A concentric cylinder cell to be used in subsequent investigations was designed and the design details are given in Appendix III. This cell can be used for the absolute measurements of the thermal conductivity of liquids at high temperatures and pressures.

3. The Constant Temperature Oil Bath

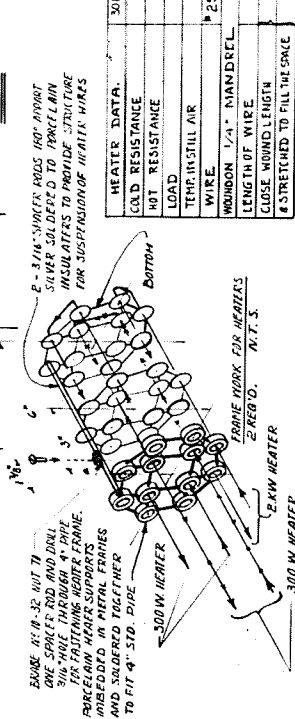
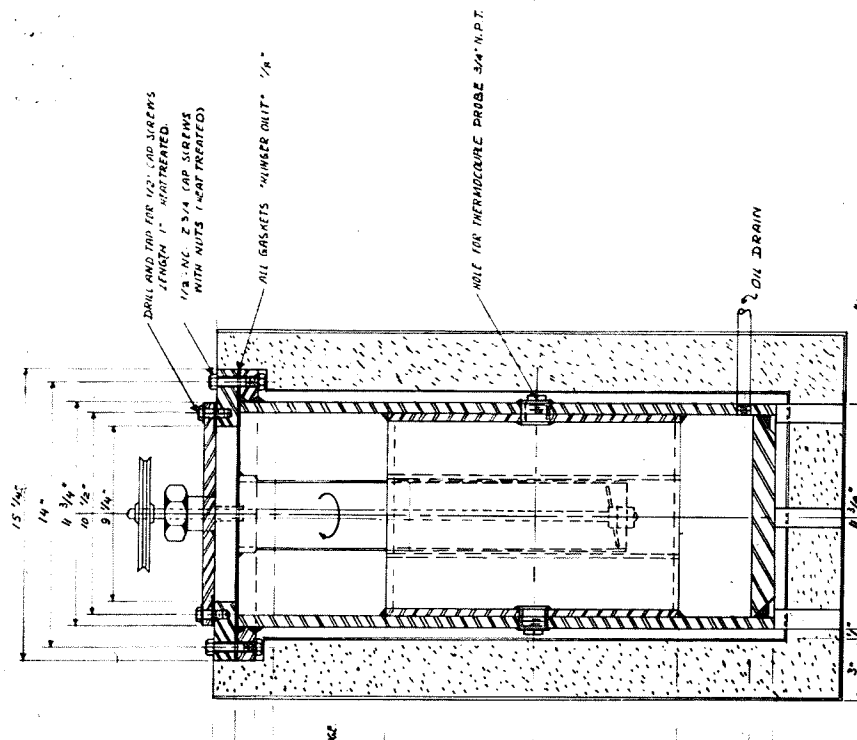
The importance of providing a constant temperature heat sink for the proper functioning of the test cells was fully realized at the beginning of the present programme. No suitable equipment with the desired temperature control was available commercially and it thus became necessary to design a suitable bath and a temperature control system. A molten salt or a liquid metal bath appeared to be an unnecessary complication due to the design temperature range from room temperature to about 800°F. A tempering oil or a silicon oil with a high flash point would cover the temperature range by slightly pressurizing the bath medium, and the design problem was consequently reduced to that of temperature control and an even temperature distribution.

For tests to be made at room temperature, a bucket of water, stirred by hand with a good sized wooden paddle, is an excellent constant temperature sink, hardly to be surpassed as concerns accuracy attainable by the most elaborate mechanism^{5,105}. For the envisaged test temperature range, however, a constant temperature oil bath was designed to operate at a maximum temperature of about 800°F and a maximum pressure of 150 psig. The bath consists essentially of three equi-length tubes, held side-by-

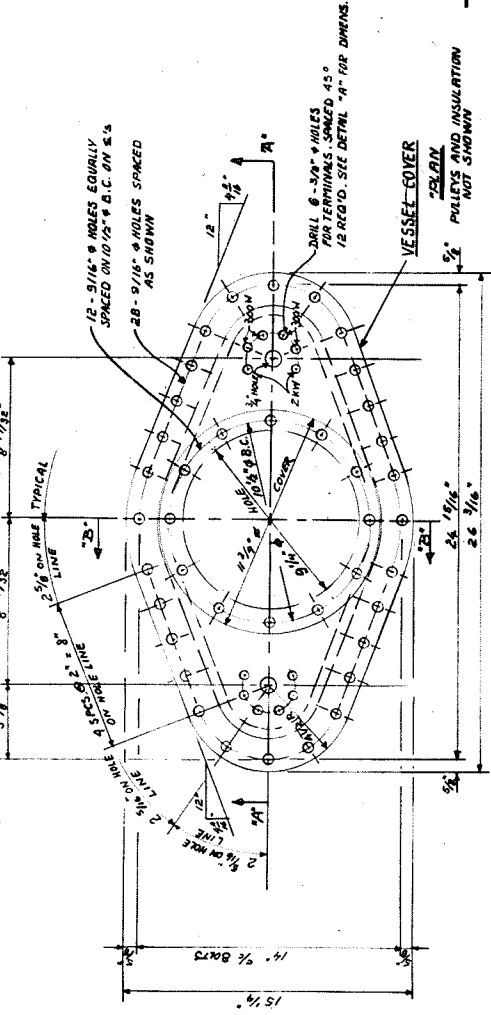
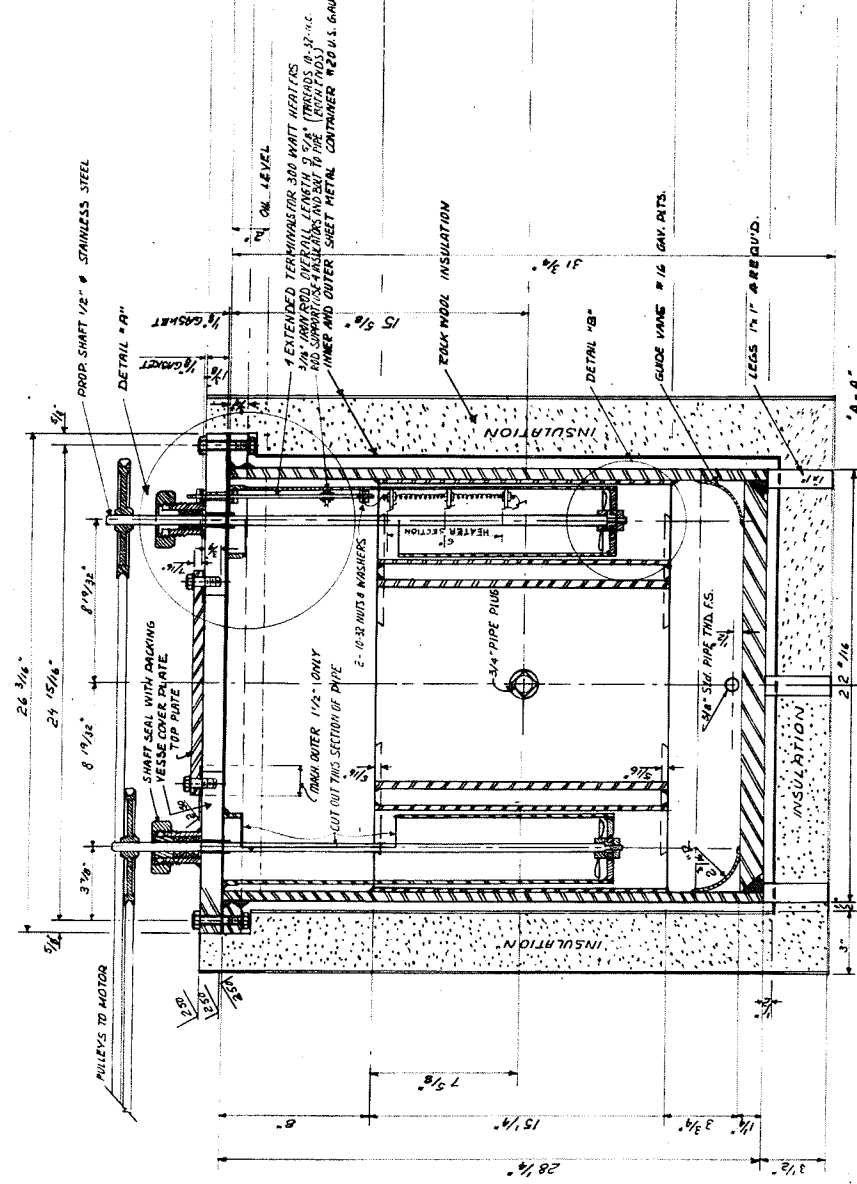
side, located in a pressure vessel at a distance of 8 inches from the open end and 3.75 inches from the base of the vessel. Fig. 2, shows the front and end, sectioned views of the bath, a plan view of the cover plates, and, details of the nichrome heating elements and the skeleton used to arrange the bath heaters. Fig. 3, shows the details of the stirrer shaft seals, the bearings and the housing for the stirrers, and, an isometric view of the pressure vessel and the cover plates. Fig. 4, shows the construction details of the pressure vessel and the cover plates and provides an itemized list of the components used. Fig. 5, shows a schematic diagram of the heaters, and, their connections, for the constant temperature bath.

The central tube is the container for the hot-wire and the concentric cylinder cells in the vertical position. This container is a 10 inch standard pipe open at both ends, and having a length of $15\frac{1}{4}$ inches. Two 4 inches diameter pipes, open at both ends, and, of the same length and material as the 10 inches diameter pipe, are rigidly fixed on either side of the central tube. Each of these two tubes contains a stirrer and a set of heaters. The concentric cylinder cell can be positioned horizontally in the space between the two stirrers at the top of the three tubes.

The heated bath medium is mixed by two motor driven screw propellers. The propellers are belt-driven by a $\frac{3}{4}$ horse power a.c. motor and rotate at about 950 R.P.M. A set of bath heaters is located above each stirrer, and the rotation of propellers is such that the bath medium first passes over the heating elements before passing through the screw



HEATER DATA.		300 W. HEATERS	PKW. HEATER
COLD RESISTANCE	44 Ω	7 Ω	
HOT RESISTANCE	42 Ω	6.5 Ω	
LOAD	2.78 AMPS.	18.2 AMPS	
TEMP. IN STILL AIR	100 °F	1100 °F	
WIRE	25 GA. 90.018	PK5 GA 9.057-	
WOUND ON	1/4" DIAM. REEL		
LENGTH OF WIRE	21 ft.	35 ft.	
CLOSE WOUND LENGTH	5"	24"	
		8 STRETCHED TO FILL SPACE	

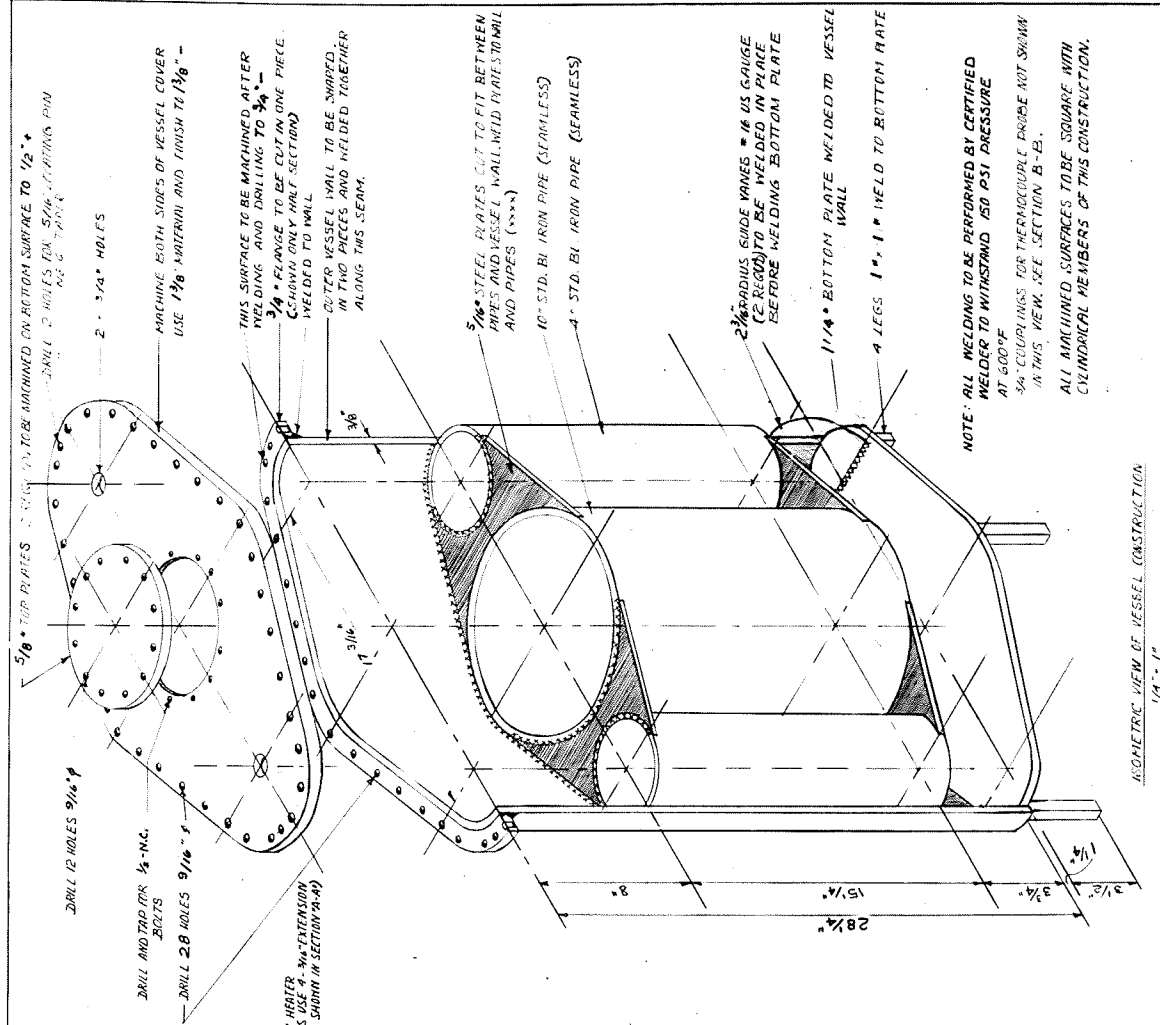


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DRAWN	24 JA	SCALE	1/4" = 1"
DATE	DEC. 11, 1962	SHEET	
APPROVED	K.C.F. BULLOCK	NO. OF SHEETS	
CONSTANT TEMPERATURE		DRAWING NO.	
OIL BATH		H 2 - 8	

REMARKS:
REVISED DRAWING.

FIG. 2.



NOTE: ALL WELDING TO BE PERFORMED BY CERTIFIED
WELDER TO WITHSTAND 150 PSI PRESSURE
AT 600° F
 $5/8" \text{ COURTLING FOR THERMO-COUPLER, PROBE NOT SHOWN}$
IN THIS VIEW. SEE SECTION B-B.

ALL MACHINED SURFACES TO BE SQUARE WITH
CYLINDRICAL MEMBERS OF THIS CONSTRUCTION.

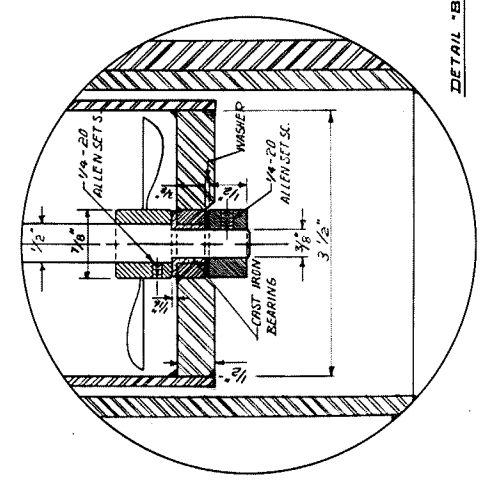
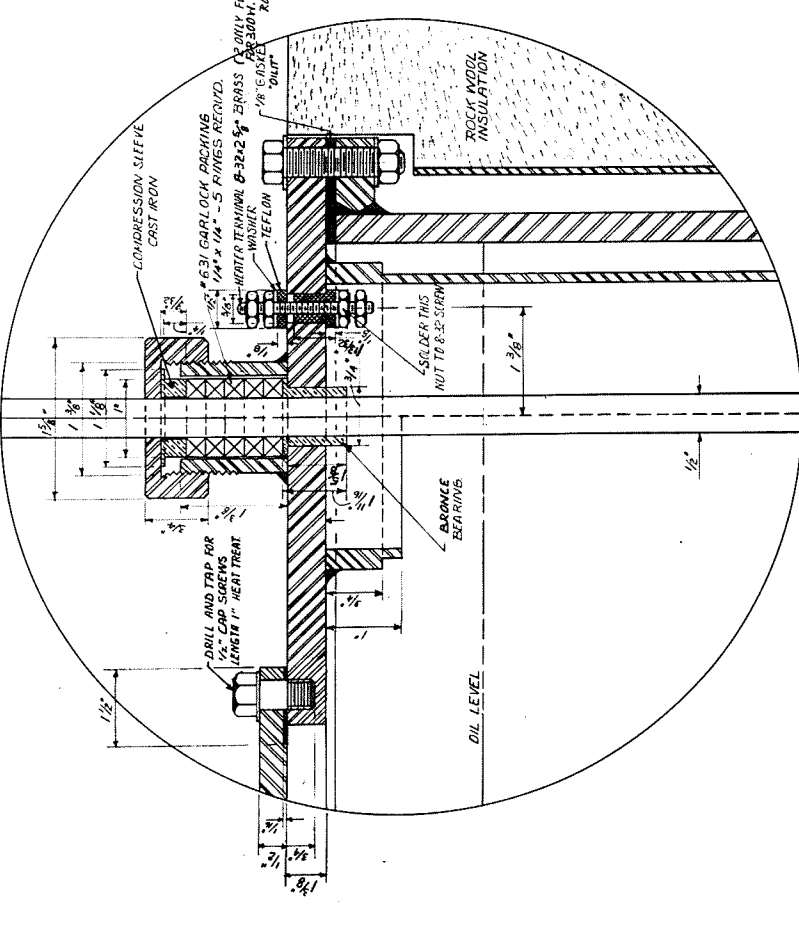


FIG. 3.

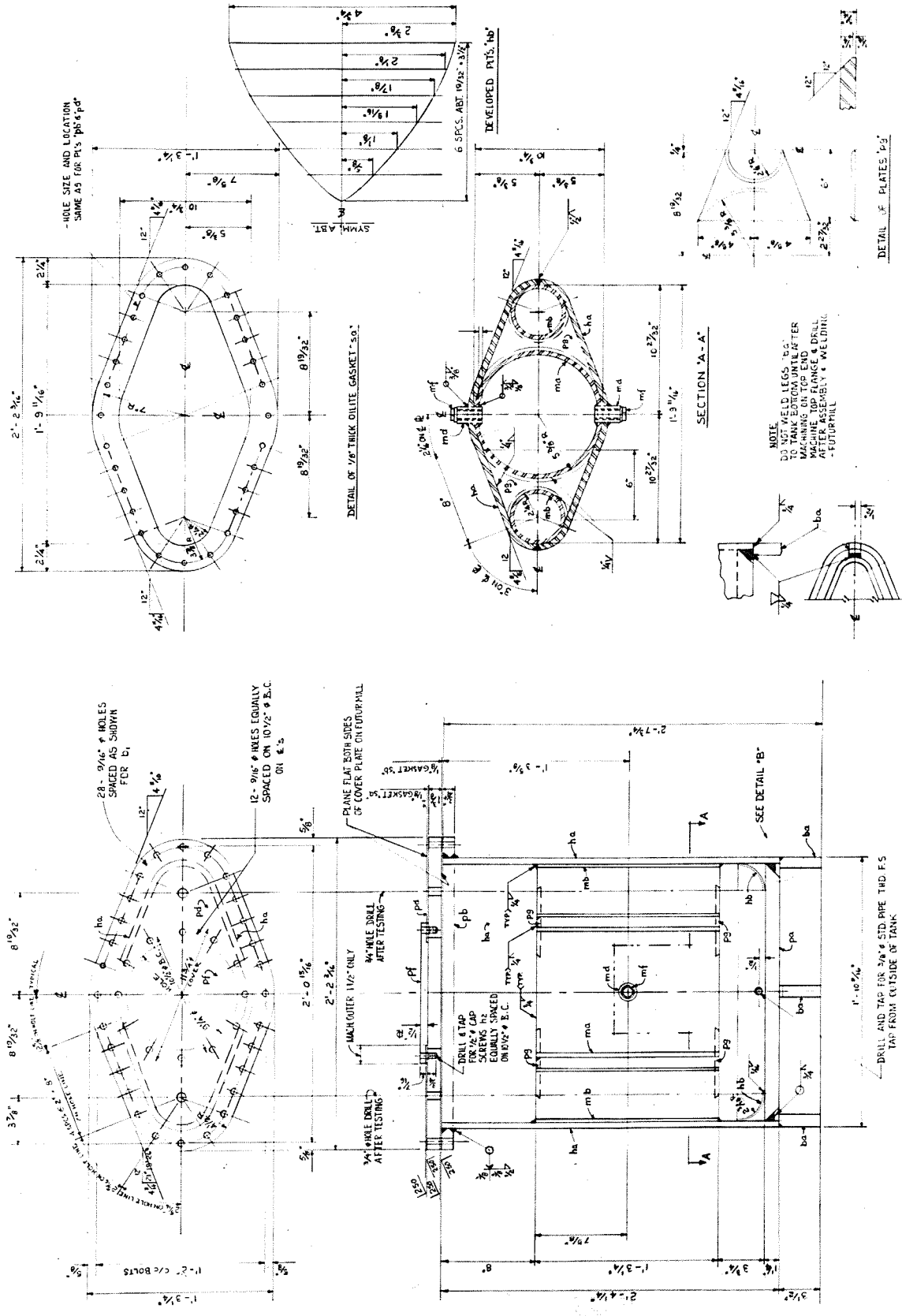
UNIVERSITY OF MANITOBA			
DEPARTMENT OF MECHANICAL ENGINEERING			
DESIGN DATE	DRAWN DATE	SCALE	SHEET NO.
APPROVED	BY	FOR	OF
CONSTANT TEMPERATURE	DRAWING NO.	OIL BATH	H 2 - 5

MARK	REQD	DESCRIPTION	LENGTH	REMARKS
		1- A1		
PA	1	10 3/4" x 1 1/4" R	1 3/4"	
PB	1	15 7/8" x 7/8" R	2 1/2"	A285 Gr C
PC	2	15 7/8" x 1 1/2" R	2 1/2"	
PD	1	11 3/4" x 3/4" R	2 1/2"	
PE	2	28 3/8" x 1/2" R's	2 1/4"	A285 Gr C F & D
PF	2	3 1/2" x 3/8" R's	4 1/4"	
PG	4	6" x 3/4" R's	3 3/4"	A285 Gr C
PH	4	1" x 1" BARS (LEGS)	3 1/2"	SAW
PI	1	10" x 1/4" STD PIPE PLAIN	1 5/8"	SUPPLIED BY
PJ	2	4" x 1/4" STD PIPE SO. ENDS	1 5/8"	UNIVERSITY
PK	2	3/4" x 4 1/2" IV OIL COUPLINGS		
PL	2	3/4" x 4 1/2" IV OIL COUPLINGS		
PM	1	15 3/4" x 1/2" OILIT GASKET	2 1/4"	
PN	1	MINOR 3/4" HOLES AS SHOWN		ANCHOR
PO	1	HEAT TREATED SAE 1038		PACKING
PP	1	HEAT TREATED SAE 1038		KLINGER
PQ	1	GASKET WITH 12 3/4" HOLES		OILIT
PR	1	HEAT TREATED SAE 1038		OILIT
PS	1	HEAT TREATED SAE 1038		OILIT
PT	1	HEAT TREATED SAE 1038		OILIT
PV	1	HEAT TREATED SAE 1038		OILIT
PW	1	HEAT TREATED SAE 1038		OILIT
PX	1	HEAT TREATED SAE 1038		OILIT
PY	1	HEAT TREATED SAE 1038		OILIT
PZ	1	HEAT TREATED SAE 1038		OILIT
QA	1	HEAT TREATED SAE 1038		OILIT
QB	1	HEAT TREATED SAE 1038		OILIT
QC	1	HEAT TREATED SAE 1038		OILIT
QD	1	HEAT TREATED SAE 1038		OILIT
QE	1	HEAT TREATED SAE 1038		OILIT
QF	1	HEAT TREATED SAE 1038		OILIT
QG	1	HEAT TREATED SAE 1038		OILIT
QH	1	HEAT TREATED SAE 1038		OILIT
QI	1	HEAT TREATED SAE 1038		OILIT
QJ	1	HEAT TREATED SAE 1038		OILIT
QK	1	HEAT TREATED SAE 1038		OILIT
QL	1	HEAT TREATED SAE 1038		OILIT
QM	1	HEAT TREATED SAE 1038		OILIT
QN	1	HEAT TREATED SAE 1038		OILIT
QO	1	HEAT TREATED SAE 1038		OILIT
QP	1	HEAT TREATED SAE 1038		OILIT
QQ	1	HEAT TREATED SAE 1038		OILIT
QR	1	HEAT TREATED SAE 1038		OILIT
QS	1	HEAT TREATED SAE 1038		OILIT
QT	1	HEAT TREATED SAE 1038		OILIT
QU	1	HEAT TREATED SAE 1038		OILIT
QV	1	HEAT TREATED SAE 1038		OILIT
QW	1	HEAT TREATED SAE 1038		OILIT
QX	1	HEAT TREATED SAE 1038		OILIT
QY	1	HEAT TREATED SAE 1038		OILIT
QZ	1	HEAT TREATED SAE 1038		OILIT

C. R. N.
MANITOBA BRIDGE & ENGINEERING WORKS
SERIAL NO 10725
SHELL SA 285 Gr C F & D TS 55,000
HEAD SA 285 Gr C TS 55,000
MINOR SA 1038 P.S.I. TENSILE STRENGTH 65,000
T-SHELL 1/2" DATE OF TEST
UW/12C
HYDROSTATK - 225 P.S.I.

SHIP WELDING	FEET	TYPE
1	3	1/4"
2	3	3/8"
3	2	1/2"
4	5	3/4"
5	12	1/2"

54



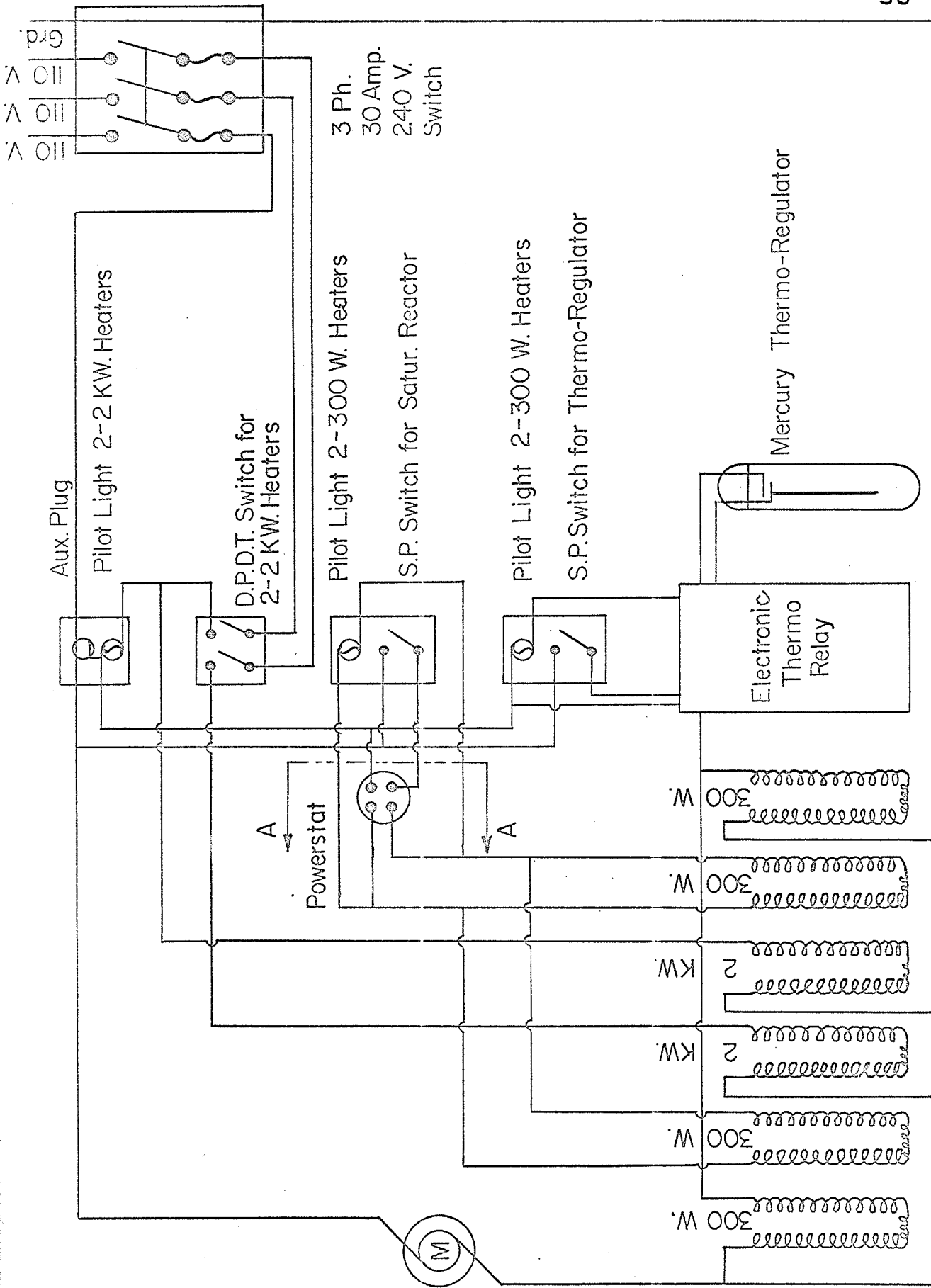
DETAIL 'A-A'

DETAIL 'B-B'

FIG. 4.

1 - PRESSURE VESSEL FOR CONSTANT TEMPERATURE OIL BATH MK 41

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TEACHING & RESEARCH ENGINEERING WORKS
DRAWING NO. M.P. 9712
SCALE 1/8" = 1'-0"
DATE 1/10/62
DRAWING NO. 92-7



Schematic Diagram of the Heaters for the Constant Temperature Bath .

FIG. 5.

propellers. The space at the bottom of stirrer tubes promotes mixing. Guide vanes are located at the corners below the stirrer tubes to prevent any dead spaces in the bath. A good temperature distribution in the bath was further insured by blanking off the spaces between the central and the stirrer tubes to provide a dead air space to prevent radial heat transfer from the heating elements to the medium in the central tube.

Each set of bath heaters consists of two separately connected 300 watt heaters and a 2 kilowatt heater. The three heaters of one set are connected in series to the corresponding heaters of the other set. This arrangement essentially provides the bath with one 4 kilowatt, and two 600 watt heaters. A pilot light was incorporated in the circuit of each set of heaters to indicate when the heaters were on. The heating elements are made from bare nichrome wire and arranged in two six inches long heater skeletons shown in Fig. 2. This figure also provides other pertinent details of the heaters.

Two mineral oils were selected as the heating media. For the test range from room temperature to about 250°F a light transformer oil was used, while for the test range from 250°F to 600°F a heavy tempering oil was used. The properties and the names of the suppliers of the two oils are given below:

(a) Transformer Oil - Volt Esso 35.

Flash Point : 290°F.

Viscosity : 58(100°F) to 34(210°F) Saybolt

Universal.

Specific Gravity : 33.5 A.P.I.

Four Point	:	-50°F.
Carbon Residue %	:	Nil
Dielectric Strength	:	30 KV
Interfacial Tension	:	40 Dynes/cm
Power Factor	:	100 V at 60 cycles 100°C - 1%
Supplier	:	Imperial Oil Refinery, Winnipeg.

(b) Tempering Oil No. 110

Flash point	:	630°F (Min)
Viscosity	:	475 - 550 S.U.S.(210°F)
Specific Gravity	:	23.5
Specific heat	:	0.4 (approx.)
Supplier	:	E.F. Houghton & Co., 100 Symes Road, Toronto 9, Ontario.

Tempering oil No. 110 is a viscous oil, green-black in colour. The oil is suitable for continuous use at temperatures up to about 350°F, but can be used in short-term tests at temperatures up to its flash point.

The bath temperature was controlled to $\pm 0.002^\circ\text{F}$ by the method to be described in the section dealing with the experimental procedure.

The bath temperature was monitored by two calibrated movable thermocouple probes, located in the bath as shown in Fig. 2. The thermocouples consist of iron and constantan conductors insulated with asbestos and fiberglass. The calibration graphs for these thermocouples are given in Appendix I.

The bath has been completely insulated to prevent heat loss

and to promote temperature uniformity. The insulation has been put in a double-walled compartment, separate from the bath, so that it can be removed easily should repairs on the bath become necessary.

This constant temperature bath is not only suitable for the steady-state thermal conductivity experiments but also ideal for accurate calibration of thermocouples and thermometers, and, any other research work requiring a constant temperature environment.

4. The Temperature Controllers

At quite an early stage of the present programme on the steady-state measurements of the thermal conductivity of liquids, it became apparent that a very sensitive temperature controller was required to control the bath temperature of at least $\pm 0.005^{\circ}\text{F}$. This magnitude of temperature control is essential for the measured thermal conductivity values to be sufficiently accurate for the envisaged small temperature difference across the test liquid layer. The degree of temperature control of the constant temperature bath is more critical than indicated in the literature. For instance, initial exploratory work⁵⁴ in U.S.A. showed that drifts of 0.001°F per minute could produce a 50 per cent error in the thermal conductivity measurements. However, cycling on the order of $\pm 0.01^{\circ}\text{F}$ with a period of a few seconds did not affect the measurements appreciably.

A complete review of the experimental work of the leading researchers in the field of thermal conductivity was carried out to ascertain the types of temperature controllers employed and the degree

of temperature control attained. Most of the authors did not specify the control limits attained on the constant temperature bath or furnace, and, dismissed this very important point by simply stating that the bath temperature was controlled closely enough so that its small cycling had no effect on the temperature drop across the test section. Some authors did state the magnitude of the temperature control attained, however, none managed to control the bath or furnace temperature to better than $\pm 0.02^{\circ}\text{F}$.

When the literature search in locating a suitable temperature controller proved to be fruitless, it was decided to contact the leading manufacturers of this kind of equipment. It was surprising to discover that none of the commercially available controllers were capable of controlling the bath temperature better than $\pm 0.02^{\circ}\text{F}$, over the desired range, for a long period. Some off-on type mercury thermoregulators are available which are capable of controlling the temperature to $\pm 0.005^{\circ}\text{F}$ at low working temperatures. One of the inherent faults of off-on temperature controllers, however, is that progressively less satisfactory performance is obtained as the desired operating temperature differs more widely from the ambient temperature.

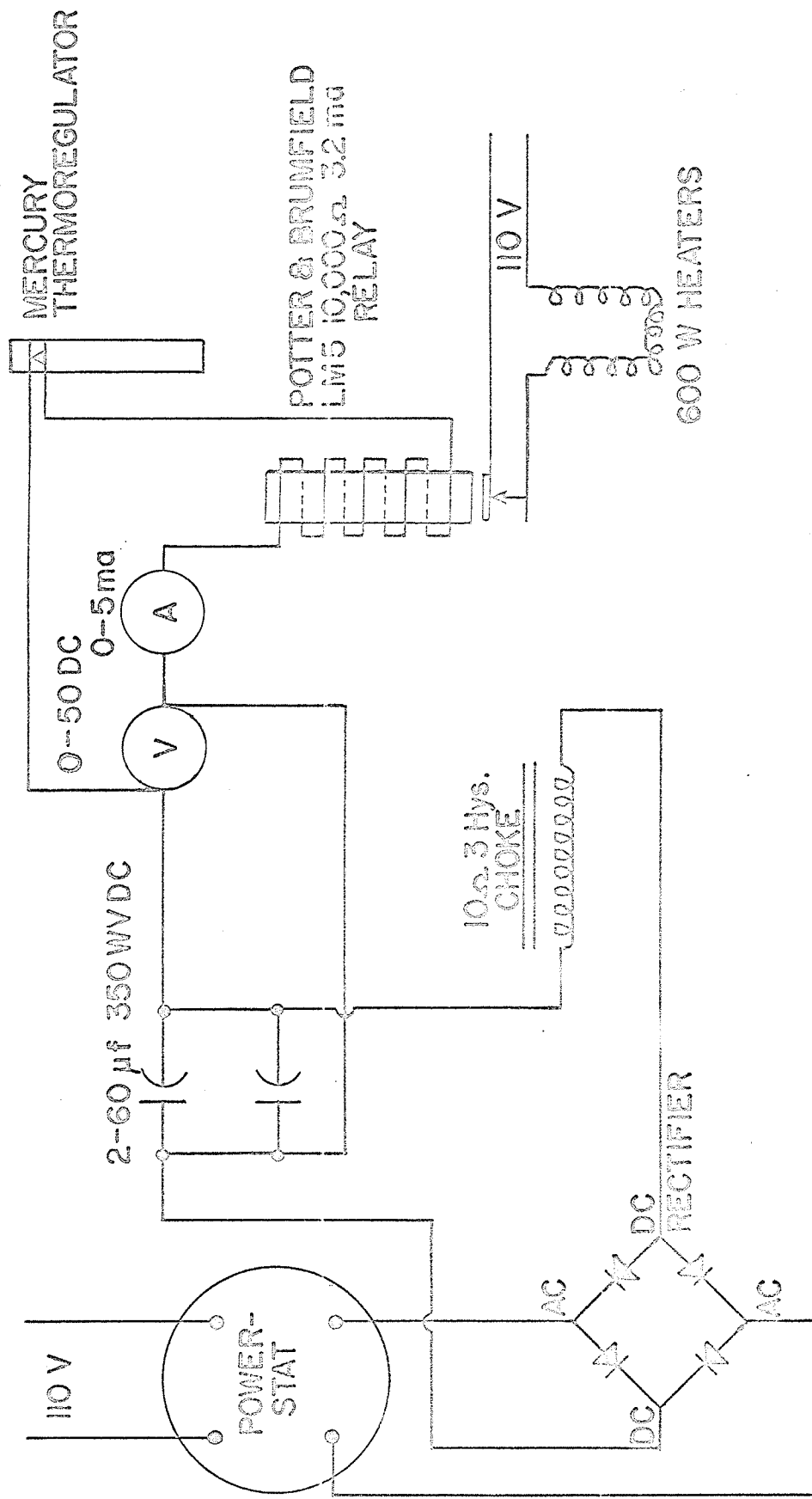
A simple mercury thermoregulator was one possible method to control the temperature to $\pm 0.1^{\circ}\text{F}$, and it was obtained to allow the familiarization runs to proceed while a more accurate temperature control covering the desired working range was developed. The result was a thermistor-type temperature controller to control temperatures to at

least $\pm 0.005^{\circ}\text{F}$. A brief description of both of these controllers is given in this section and Appendix III.

(a) The Mercury Thermoregulator.

This regulator was used to control the bath temperature to $\pm 0.1^{\circ}\text{F}$, in conjunction with a relay. The regulator is essentially a contact making thermometer with an adjustable range from -35°F to 700°F , having a sensitivity of $\pm 0.1^{\circ}\text{F}$. It consists of a large mercury bulb with fine capillary tube outlet. The upper bulb serves as a reservoir for the surplus mercury. The mercury rising in the capillary stem contacts first one platinum wire and then the second, thus completing the electrical circuit without movement of the electrodes themselves.

A voltage of 30 volts d.c. or a direct current of 3 milliamperes, across the input terminals, will operate the relay. The designed relay, shown in Fig. 6, supplies 110 volts a.c. to one set of two 300 watt heaters. A pilot light incorporated in this 600 watt heater system lights up when the heaters are on and goes off when no heat is being supplied to the bath. The operation of the relay is straight forward. Approximately 30 volts from the 110 volts a.c. line are supplied to the input terminals of the relay through a powerstat and a simple rectifier bridge circuit. Before the rectified voltage is supplied to the relay, however, it is passed through two 60 micro-farad capacitors, connected in parallel, which block any superimposed a.c., and, a choke, which has a resistance of 10 ohms and an inductance of 3 Henries, to smooth out any ripple in the rectified voltage. A d.c. voltmeter and a milliammeter



SCHEMATIC FOR ELECTRONIC RELAY.

FIG. 6.

are positioned in the relay circuit to check the voltage and the direct current being supplied to the relay. The relay has a resistance of 100,000 ohms with a current rating of 3.2 milliamperes, d.c.

The relay is constructed such that when no current is flowing through the relay coil, the 600 watt heater contacts remain closed, and heat is supplied to the bath. When the oil in the bath has reached the desired temperature, the rising mercury in the thermoregulator capillary contacts the second platinum electrode, thus completing the electrical circuit and operating the relay. As soon as the electrical circuit is completed, the main contacts to the 600 watt heater are opened and no more heat is supplied to the bath till the temperature falls 0.1°F from the set temperature. The thermoregulator must be pre-set to the desired control temperature.

(b) Design of the Thermistor-Type Temperature Controller

An electronic temperature controller incorporating a thermistor was designed and the details are given in Appendix III. The construction of the controller could not be completed in time to make its use possible in the reported work. However test runs performed at a later date showed that the temperatures could be controlled to $\pm 0.005^{\circ}\text{F}$ with this controller. The controller, however, can only be used within the range from room temperature to about 600°F as thermistors become unreliable after 600°F ¹⁶.

5. The Arc Welding Apparatus

The thermocouples selected to measure the temperature difference across the liquid layer in the concentric cylinder cell were the "Ceramo" duplex conductor type thermocouples. The "Ceramo" thermocouples consist of two 0.010 inch diameter wires of compatible thermocouple material contained in a 0.040 inch diameter stainless steel sheath. The space between the wires and the sheath is packed with a ceramic or inert metal oxide insulation to insulate the wires from each other and from the sheath. The stainless steel sheath protects the thermocouples from pressure and chemical action of the liquids to be investigated.

A special apparatus for affecting the union between the wires was necessary as conventional flame welding methods are unsuitable due to the small size of the wires. The apparatus design and construction details are given in Appendix III.

VI : CALIBRATIONS AND EXPERIMENTAL PROCEDURE

Prior to the test runs with the organic liquids, it was necessary to calibrate the test section of the hot-wire cell and the bath thermocouples, for the temperature measurements. The calibrations were performed with a precision platinum resistance thermometer, recently calibrated⁹⁸ by the National Research Council, Ottawa.

It was planned initially to use calibrated thermocouples for the bath temperature measurements in the course of the test runs. During the calibration runs, however, it was realized that the temperatures could not be measured to the desired accuracy with thermocouples. The calibrated resistance thermometer was, consequently, used for all temperature measurements during the test runs.

Section A : Calibrations and Methods of Measurements

1. Temperature Measurements.

The calibrations and the bath temperature at all the test points were determined with a Leeds and Northrup precision, four-lead, platinum resistance thermometer, number 8163. The thermometer was calibrated⁹⁸ by the National Research Council, Ottawa, from -183°C to 630°C .

Temperatures corresponding to the measured resistances of the thermometer were computed by using the methods given by Schwab and Smith¹³². For a temperature range of 0°C to 660°C , the temperature measured by the resistance thermometer can be calculated to within the

precision of calibration, by a single computation on a calculating machine. This single computation is only possible if the temperature can be estimated to within 1°C of the actual temperature. Temperature resistance plots were made by calculating values of " R_t " for " t " equal to various temperatures within the test range from the fundamental formula for the resistance thermometer, $R_t = R_0 (1 + At + Bt^2)$.

'A', 'B' and ' R_0 ' are the thermometer constants determined by calibration⁹⁸. These graphs were used to estimate the temperature corresponding to the measured resistance of the thermometer, and then the actual temperature was calculated by substituting the estimated value into the formula given by Schwab and Smith.¹³²

A Mueller Temperature Bridge⁹⁵, in conjunction with a Mercury Commutator⁹³, was used to measure the thermometer resistance.

The Leeds and Northrup Mueller Temperature Bridge, number 8067, is a precision instrument designed to measure temperature or temperature differences to a high degree of accuracy. The instrument is essentially a Wheatstone bridge and measures resistance or resistance differences; which in turn permits determination of temperature or temperature differences. Errors due to contact resistance in the step-by-step switches used in the instrument, are reduced to a negligible value by shunting the switches and series resistors (of comparatively high resistance) with resistors having low resistance values. The maximum resistance which can be measured by the bridge is 81.111 ohms and the instrument reads to 0.001 ohm.⁹⁵

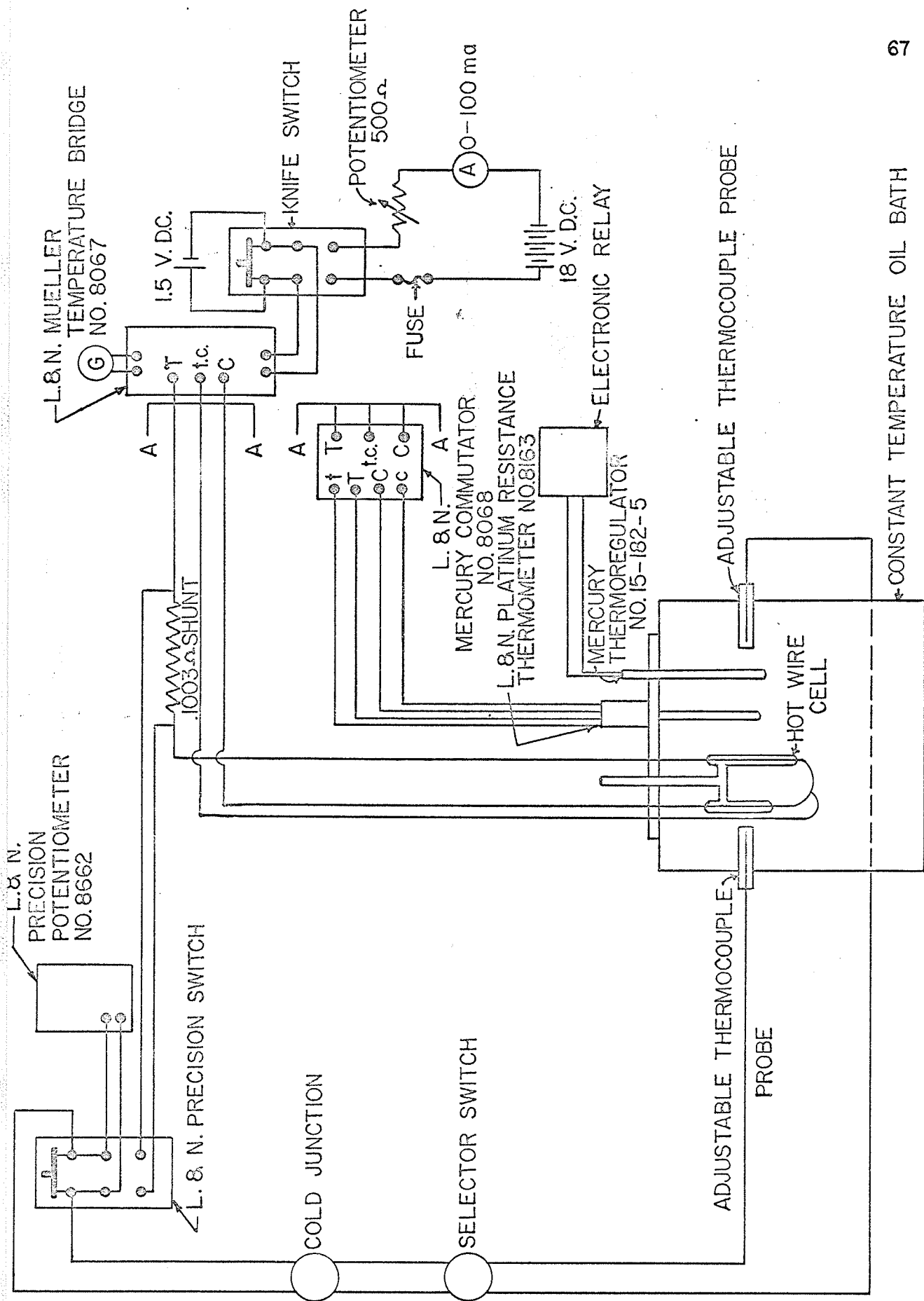
Since the thermometer used is a potential lead platinum resis-

tance thermometer, a three pole double throw knife switch or a mercury commutator is required as a switching device. A Leeds and Northrup Mercury Commutator, number 8068, was employed for this purpose. The commutator provides a simple and rapid means of nullifying the effect of unequal lead resistance, a precaution necessary when making precise temperature measurements with a resistance thermometer of the potential lead type. To nullify the effect of unequal lead resistance two readings, one with the mercury switch in the "normal" and the other with the mercury switch in the "reverse" position, were taken at each temperature setting. When making temperature measurements, the t, T, C and c terminals of the thermometer were connected respectively to the t, T, C and c terminals of the mercury commutator. The T, t, c, and C terminals of the mercury commutator were connected in turn to the T, t, c, and C terminals of the Mueller bridge. A honeywell-Brown null detector was used to ascertain the bridge balance. The bridge was energized by two 1.5 volt dry cells connected in parallel and supplying approximately 3 milliamperes direct current to the bridge. Fig. 7 shows a schematic of these connections.

The temperature - resistance relationship for the resistance thermometer, as measured during the course of the test runs, is shown in the graphs of Set A. These graphs can be found in Appendix I.

2. Temperature Control of The Bath.

During the familiarization runs with the equipment, a unique yet simple method of controlling the bath temperature was discovered. This method has been very successful during the course of the present work



SCHEMATIC OF THERMAL CONDUCTIVITY MEASUREMENT APPARATUS FOR ORGANIC LIQUIDS.

FIG. 7.

and has enabled the temperature to be controlled to $\pm 0.002^{\circ}\text{F}$ over the range 75°F to 603°F . The procedure for obtaining this control is straight forward. The platinum resistance thermometer is used for the temperature measurements and its approximate resistance corresponding to any particular temperature is obtained from the graphs of Set A provided in Appendix I. Since the Mueller Temperature Bridge is used to measure the resistance of the thermometer, the approximate resistance determined from the appropriate graphs, is pre-set on the bridge. This procedure permits a continuous monitoring of the bath temperature on the null detector connected to the bridge. The mercury thermoregulator is inserted in the bath and connected, through the relay, to one set of the 600 watt heaters. All the heaters are then turned on and the bath medium heated to the desired temperature. When this temperature is reached all the heaters, except the set of 600 watt heaters controlled by the thermoregulator are turned off. The bath is allowed to reach the state where its temperature is controlled to $\pm 0.1^{\circ}\text{F}$ by the thermoregulator. When this degree of temperature control is attained, the period of the off-on cycle of the 600 watt heaters is measured by observing the pilot light on the switch panel of the bath heaters. From the measured cycle the approximate heat loss from the bath is calculated, and this loss supplied continuously by the second set of 600 watt heaters. The electrical input to this set of heaters is supplied through a manually operated variac. After a settling period, final adjustments of the variac are made until there is zero deflection on the null detector. In this manner the bath temperature can be controlled to $\pm 0.002^{\circ}\text{F}$ for a

long period. During the course of tests, if the null detector pointer did not move from its zero position for about an hour, the bath was assumed to have reached the equilibrium state.

It is felt, however, that the bath temperature control is even better than $\pm 0.002^{\circ}\text{F}$ due to the inherent stability of the bath. The available Mueller bridge can only measure the resistance to 0.0001 ohm. A change of 0.0001 ohm in the resistance of the platinum thermometer corresponds to a change of 0.00178°F in the temperature of the bath medium. If an additional step-by-step switch was available on the Mueller bridge, the bath temperature could easily be controlled to $\pm 0.001^{\circ}\text{F}$.

3. Calibration of the Bath Thermocouples.

Two iron-constantan thermocouples, made into adjustable probes, were installed in the bath. The probes were made both leak proof and pressure tight to permit their use if the bath medium is pressurized. The thermocouples were connected to a twenty point selector switch. The cold junction of the thermocouples was kept at ice point (32°F). The potential-carrying leads from the selector switch were attached to a potentiometer through a double-pole, double-throw, precision instrument switch.

The e.m.f. generated by the thermocouples is measured by a precision Leeds and Northrup potentiometer¹⁰⁶, number 8662. The generated e.m.f. can be measured accurately to 0.01 millivolt and estimated to 0.002 millivolts with good accuracy.

The calibration data and graphs for the bath thermocouples are

given in Appendix I. The temperature-millivolt relationship is shown in the graphs of Set B in the appendix.

4. Calibration of the Test Section for the Temperature Measurements.

The filaments in the short and the long limbs of the hot wire cell were connected in series. A copper lead was attached at the middle of the lead joining the two filaments thus providing an arrangement analogous to a two lead differential resistance thermometer. The final reading is the difference between the resistance of the two filaments, and, this resistance is measured directly on the Mueller bridge. Two copper extension leads of equal length were attached to the free end of each filament. The three leads were connected to the Mueller bridge as shown in Fig. 7, page 67.

The test range for Carbon Tetrachloride and Toluene was from about 68°F to near their respective boiling points, while the range for HB-40 and Hydrogenated Santowax OM was from about 250°F to about 600°F. The temperatures at which the thermal conductivities of the four liquids were to be measured, were selected. Prior to filling, the cell was thoroughly cleaned with solvents and evacuated in order to eliminate contamination of the test liquids. For the calibration range from 68°F to about 230°F the cell was filled with Toluene. The level of the liquid in the cell was such that both the filaments were completely immersed. The cell was then immersed in the bath and the oil heated to about 5°F below the temperature at which the conductivity measurement was to be made. The bath temperature was controlled to $\pm 0.002^\circ\text{F}$ at this tempera-

ture, and resistance of the test section measured with the Mueller bridge. The bath was then heated to the temperature at which the conductivity value was required and the resistance of the test section measured again. Similar procedure was carried out at a temperature 5°F above the selected test temperature. This procedure was repeated to provide accurate resistance of the test section at 5°F below and above each temperature selected for a thermal conductivity measurement.

After the calibration of the test section for the temperature measurements had been completed to about 230°F , the cell was emptied, thoroughly cleaned with solvents, evacuated for a long period, and then refilled with HB-40. Since HB-40 has a boiling range between $644 - 744^{\circ}\text{F}$, it was used to provide the required constant temperature environment in the cell for calibration of the test section between 250°F and about 600°F .

The graphs of Set C in Appendix I show the temperature-resistance relationship for the test section.

5. Measurement of the Power Supplied to the Test Section

For accurate determination of the thermal conductivity of a test liquid, the heat dissipated by the test section of the cell must be measured very accurately. The heat to the test section was supplied in the form of direct current from 6 and 12 volt storage batteries, connected in series. Although d.c. milliammeters are available for such measurements, it was felt that since the power dissipated by the test section would be quite small, a more accurate and reliable method was warranted. The method used is briefly outlined in this section.

The electrical power supplied to the test section was determined from accurate measurements of the heating current and the resistance of the test section when the filament was dissipating heat at steady state. It was therefore necessary to make both measurements simultaneously.

The resistance of the test section of the cell was measured directly on the Mueller bridge. The cell was connected to the bridge in the manner similar to that for the calibration of the test section described in section VI.4. Since the Mueller bridge is essentially a Wheatstone bridge, the cell filaments formed one ratio arm of the bridge. Therefore the heating current that could be supplied to the cell was limited by the bridge. To prevent damage to the bridge, the maximum current was about 72 milliamperes. Since the filaments in both limbs of the cell were connected in series, the cell current was thus limited to 36 milliamperes.

The current supplied to the cell was determined from measuring the voltage drop across a precision manganin resistor connected in series with the test section filament (see Fig. 7). The resistance of the manganin resistor was accurately predetermined on a precision Kelvin bridge in the Standards Laboratory, Department of Electrical Engineering, University of Manitoba.

The thermal energy dissipated by the test section was consequently determined from the electrical power supplied to the test section.

Section B : Experimental Procedure

Carbon tetrachloride and Toluene were tested as received from the manufacturer, and, HB-40 and Hydrogenated Santowax OM were tested as received from the Atomic Energy of Canada Limited. Prior to each filling with the test liquid, the cell was thoroughly cleaned by the procedure previously described. When filling, caution was taken to make sure that the level of the liquid was sufficient to completely immerse the filaments.

The filled cell was suspended in the oil bath but the filament leads were not connected to the Mueller bridge. The various instruments and their connections as used in the thermal conductivity tests are shown schematically in Fig. 7.

After the cell was mounted in the oil bath, the platinum resistance thermometer and the mercury thermoregulator were positioned. The resistance thermometer was connected to the Mueller bridge through the mercury commutator, and, the mercury thermoregulator was connected to the electronic relay, thus controlling one set of 600 watt heaters. The Mueller bridge was pre-set to measure the resistance the thermometer will have at the temperature the test was to be performed. The bridge was energized by the 1.5 volt d.c. batteries. The bath heaters were then turned on and the oil heated to the desired test temperature. When the oil reached the set temperature all the heaters, except the set of 600 watt heaters controlled by the thermoregulator, were turned off. The bath was then allowed to reach a steady temperature as

determined by the preset thermoregulator. Using the method described in section VI, 2, page 68, the heat losses from the bath were accurately compensated for and if the bath temperature did not vary by more than $\pm 0.002^{\circ}\text{F}$ over a period of about one hour, the bath and the cell were assumed to have reached the steady state.

Once the steady state was established, the resistance thermometer leads were disconnected from the Mueller bridge and the bath temperature monitored throughout the test period by the two calibrated thermocouples. The Mueller bridge was then used to measure the resistance of the test section filament prior to the application of the heating current. The batteries supplying the current for heating were connected and a heating current passed through the filaments and the Mueller bridge to determine the resistance of the filament during the test. The exact magnitude of the cell current was ascertained by measuring the voltage drop across the 0.1003 ohm precision resistor connected in series with the test section filament by means of the precision potentiometer. The resistance of the test section was continuously checked when the heating current was passing through it, and, when it did not vary over a period of about 15 to 20 minutes, the steady-state heat transfer by conduction was assumed to have been established. At this steady-state, the resistance of the filament and the heating current passing through it were accurately measured. The storage batteries and the cell leads were then disconnected, and the resistance thermometer re-connected to the bridge through the mercury commutator. After completing the thermal conductivity test, the bath temperature

was re-checked, and, if it has varied by more than $\pm 0.002^{\circ}\text{F}$, all the data accumulated for that test was rejected.

The bath was then heated to the next test temperature and the foregoing procedure repeated for securing the relevant data at that temperature. The temperature of the room was kept relatively constant, and sufficient time allowed between the tests for the test section filament to reach the same temperature as the bath.

Fig. 8 on the next page, shows a general photographic view of the thermal conductivity apparatus.

Appendix II contains the experimental data and the available physical properties of the four organic liquids tested.



GENERAL VIEW OF THE THERMAL CONDUCTIVITY APPARATUS

FIG. 8 .

VII : DATA ANALYSIS AND CALCULATION OF THERMAL CONDUCTIVITY

If q Btu of heat per hour are supplied by the filament, a steady state is reached where

$$q = \frac{2\pi L K_{\text{liq}} (T_f - T_i)}{\ln \frac{r_i}{r_f}} \dots\dots\dots (\text{VII.1})$$

As this cell is placed in the bath, a constant temperature, T_b , is maintained at the outer surface of the glass tube. This temperature is not the same as that at the inner surface of the tube; consequently, a correction must be made for the temperature drop through the glass wall. Since the quantity of heat conducted through the liquid in the cell is also conducted through the glass wall to the oil in the bath, the following equation applies:

$$q = \frac{2\pi L K_g (T_i - T_b)}{\ln \frac{r_o}{r_i}} \dots\dots\dots (\text{VII.2})$$

Combining equations (VII.1) and (VII.2), equation (VII.3) is obtained, which is used for evaluating the thermal conductivity of the liquid being investigated:

$$\frac{T_f - T_b}{q} = \frac{1}{2\pi L K_{\text{liq}}} \ln \frac{r_i}{r_f} + \frac{1}{2\pi L K_g} \ln \frac{r_o}{r_i} \dots\dots\dots (\text{VII.3})$$

This equation may be written as follows:

$$\frac{\Delta T}{q} = \frac{A}{K_{\text{liq}}} + \frac{B}{K_g} \dots\dots\dots (\text{VII.4})$$

Where A and B are constants dependent only on the dimensions and material of construction of the apparatus. ΔT is determined from measuring the bath and the test section temperatures under test conditions. The quantity of heat conducted, q , is ascertained from measuring the test section resistance and the quantity of direct current passing through the cell. Thus $\frac{\Delta T}{q}$, obtained from actual measurements in conjunction with the cell constants A and B, enabled K_{liq} to be calculated.

Equation (VII.4) assumes that there is no significant temperature difference between the outer wall of the glass tube and the bath liquid. This condition could not be met but with low heat fluxes and the following precautions its effects were kept to a minimum. Before passing any electric current through the test section of the cell it was necessary to establish steady state conditions. The cell containing the test liquid was immersed in the bath and the bath heated to the desired temperature. The platinum resistance thermometer was used to measure and control bath temperatures as outlined in section VI. The test section of the cell and the adjustable thermocouple probes had previously been calibrated by using the resistance thermometer. At steady state the temperature of the liquid in the cell was determined by measuring the resistance of the test section and this temperature was equal to the bath temperature in each case. The resistance thermometer was always located close to the unit of the cell containing the test section. At steady state conditions the resistance thermometer was moved up and down to check any temperature variations in the bath. The adjustable thermocouple probes had been made sufficiently long so that

they could touch the outside of the unit of the cell containing the test section. Again at steady state these probes were moved across the bath to check any temperature variations in the horizontal plane. When the electric current was passed through the test section at experimental conditions, the adjustable thermocouple probes were always in contact with the outside of the glass tube. These probes, however, were not sensitive enough to permit any predictions to be made as to the temperature of the glass.

There is a large uncertainty in the thermal conductivity of the glass (K_g). The published values for the thermal conductivity of various glasses are far from being consistent, since serious technical difficulties are encountered in measuring this value accurately. The manufacturers of the glass from which the cell is fabricated, Corning Glass Works, Corning, New York, were contacted regarding the availability of accurate values of K_g ^{33,34}. Only three values of K_g at 77°F, 392°F, and 752°F were provided by the Corning Glass Works, and the thermal conductivities of the glass at other temperatures were interpolated linearly from these values. The geometry of the cell is such that a 20% error in K_g only results in a 1% error in the calculated values of K_{liq} .

The following expressions show the manner in which the cell constants A and B depend on the dimensions of the apparatus.

$$A = \frac{1}{2\pi L} \ln \frac{r_i}{r_f}$$

$$B = \frac{1}{2\pi L} \ln \frac{r_o}{r_i}$$

The values of A and B depend on the effective length of the test section filament, the effective radius of the filament, and, the inside and outside radii of the glass tube. The inside and outside diameters of the glass tube were accurately measured and are as follows:

Inside diameter, $d_i = 0.3937$ in.

Outside diameter, $d_o = 0.4785$ in.

The mean effective diameter of the filament were arrived at in the following manner. The test section filament was fabricated from 0.0034 inch diameter Tungsten wire and was wound on a 0.0505 inch core. After removing the winding core the outside diameter of the filament was measured to be 0.0600 inch. The pitch of the filament was 174 turns per inch. It was necessary to make the pitch small because if pitch is too large three-dimensional heat flow effects could occur locally which would lead to errors in the experimental values of the thermal conductivity of the liquids tested. From this data the mean effective diameter of the filament was calculated as outlined below.

Effective filament diameter = winding core dia. + dia. of
Tungsten wire.

= (0.0505 + 0.0034) in.

= 0.0539 in.

The effective filament
diameter is also

= outside diameter of filament
- dia. of Tungsten wire.

$$\begin{aligned}
 &= (0.0600 - 0.0034) \text{ in.} \\
 &= 0.0566 \text{ in.} \\
 \text{Mean effective diameter} &= \frac{0.0539 + 0.0566}{2} \\
 \text{of filament} & \\
 &= 0.05525 \text{ in. } \pm 2.6\%
 \end{aligned}$$

The mean effective length of the test section was calculated as follows. The cold resistances of both the filaments were measured before and after they were sealed in their respective limbs. The test section length was calculated for each case, and the average taken to obtain the mean effective length.

Calculation of Test Section Length Before Sealing Filaments in the Limbs:

$$\begin{aligned}
 \text{Resistance of the filament in the short limb} &= 5.536 \text{ ohms} \\
 \text{Specific resistance of this filament} &= \frac{5.536}{1.973} \text{ ohms per in.} \\
 &= 2.805 \text{ ohms per in.} \\
 \text{Resistance of the filament in the long limb} &= 11.503 \text{ ohms.} \\
 \text{Specific resistance of this filament} &= \frac{11.503}{4.099} \text{ ohms per in.} \\
 &= 2.806 \text{ ohms per in.} \\
 \therefore \text{Length of the test section} &= \frac{11.503 - 5.536}{2.806} \text{ ins.} \\
 &= 2.1263 \text{ ins.}
 \end{aligned}$$

Calculation of Test Section Length After Sealing Filaments in the Limbs:

$$\begin{aligned}
 \text{Resistance of filament in the short limb} &= 5.539 \text{ ohms} \\
 \text{Resistance of filament in the long limb} &= 11.903 \text{ ohms} \\
 \text{Specific resistance of this filament} &= \frac{11.903}{4.099} \text{ ohms per in.}
 \end{aligned}$$

$$\begin{aligned}
 &= 2.90388 \text{ ohms per in.} \\
 \therefore \text{Length of the test section} &= \frac{11.903 - 5.539}{2.90388} \text{ ins.} \\
 &= 2.1916 \text{ ins.} \\
 \text{Mean Effective Length of the test section} &= \frac{2.1263 + 2.1916}{2} \text{ ins.} \\
 &= 2.1589 \text{ ins. } \pm 1.5\% \\
 &= 0.1799 \text{ ft.}
 \end{aligned}$$

The cell constants A and B were then calculated as shown below:

$$\begin{aligned}
 A &= \frac{1}{2\pi L} \ln \frac{r_i}{r_f} = \frac{1}{2\pi L} \ln \frac{d_i}{d_f} \text{ ft.}^{-1} \\
 &= \frac{1}{2 \times 0.1799 \times \pi} \ln \frac{0.3937}{0.05525} \text{ ft.}^{-1} \\
 &= 1.7371903 \text{ ft.}^{-1} \\
 &= 1.7372 \text{ ft.}^{-1} \pm 3.5\%
 \end{aligned}$$

$$\begin{aligned}
 B &= \frac{1}{2\pi L} \ln \frac{r_o}{r_i} = \frac{1}{2\pi L} \ln \frac{d_o}{d_i} \text{ ft.}^{-1} \\
 &= \frac{1}{2\pi \times 0.1799} \ln \frac{0.4785}{0.3937} \text{ ft.}^{-1} \\
 &= 0.17256015 \text{ ft.}^{-1} \\
 &= 0.1726 \text{ ft.}^{-1} \pm 1.5\%
 \end{aligned}$$

The accuracy of the value of the thermal conductivity depends on the accuracy with which the filament temperature can be calculated when it is dissipating heat. Three separate test runs were performed with Carbon Tetrachloride and Toluene, and, two with HB-40 and Hydrogenated Santowax CM. The test section resistance, with no heating current through it, had already been established at each desired test tempera-

ture and at 5°F below and above this particular temperature, and the data plotted accurately to obtain the average temperature slope, $^{\circ}\text{F}$ per ohm, for each test temperature of each liquid. At test conditions, the bath temperature was measured with the precision resistance thermometer. Since no heating current was passed through the cell at this state, the test section was at the same temperature as the bath and its resistance was measured on the Mueller bridge. The test section resistance was measured when the heating current was on and the steady state heat transfer thus established. The increase in the test section resistance was then obtained and ΔT , the difference between the filament and the bath temperatures, was calculated from the relevant average temperature slope.

A specimen calculation for HB-40, shown below indicates the procedure adopted to calculate the thermal conductivity of the liquids. The procedure is illustrated for the test at 350.33°F .

Average applicable temperature slope calculated from the calibration data	= 67.5°F per ohm
Increase in resistance of the test section when heating current passed	= 0.0175 ohm
$\therefore \Delta T$, difference in the filament and the bath temperature	= $67.5 \times 0.0175^{\circ}\text{F}$ = 1.181°F
Voltage drop across the 0.1003 resistor	= 3.631 millivolts
Current through the test section	= $\frac{3.631}{0.1003}$ amps = 36.2014×10^{-3} amps.
Resistance of the test section when dissipating heat	= 10.2437 ohms

$$\begin{aligned} \text{Electrical power dissipated by the} & & & = (36.2014 \times 10^{-3})^2 \\ \text{test section} & & & \times 10.2437 \quad \text{watts.} \\ & & & = 134.2479 \times 10^{-4} \text{ watts} \end{aligned}$$

$$\begin{aligned} \text{Thermal energy dissipated by the} & & & = 134.2479 \times 10^{-4} \\ \text{test section} & & & \times 3.41297 \quad \text{Btu/Hr} \\ & & & = 458.184 \times 10^{-4} \text{ Btu/Hr} \end{aligned}$$

$$\text{Thermal conductivity of glass at } 350.33^\circ\text{F} = 0.745 \text{ Btu}/(\text{Hr})(\text{Ft})(^\circ\text{F})$$

Substituting relevant values into Equation (VII.4)

$$\frac{1.1812}{458.18 \times 10^{-4}} = \frac{1.7372}{K_{\text{liq}}} + \frac{0.1726}{0.745}$$

$$K_{\text{liq}} = 0.068 \text{ Btu}/(\text{Hr})(\text{Ft})(^\circ\text{F})$$

$$\therefore \text{Thermal Conductivity of HB-40 at } 350.33^\circ\text{F} = 0.068 \text{ Btu}/(\text{Hr})(\text{Ft})(^\circ\text{F})$$

A similar procedure was applied to calculate the thermal conductivity of all other liquids at their respective temperatures.

Graphs in the next section show the absolute thermal conductivity versus temperature relationship for the four organic liquids tested during the course of this work.

The experimental thermal conductivity values and other relevant experimental data, as well as the available physical properties of the liquids investigated, are contained in Appendix II.

VIII : PRESENTATION OF THE RESULTS

The thermal conductivity values for the four organic liquids tested were calculated in the manner outlined in the section on data analysis and calculations. The experimental values thus evaluated are plotted against temperature and the resulting graphs are contained in this section. For easy reference, the test temperatures and the corresponding thermal conductivity values for each liquid are given in a tabular form.

The thermal conductivity of Carbon Tetrachloride and Toluene at various temperatures are available in the literature, and those values which are considered to be the most reliable are plotted on the graphs showing the results of this work.

No experimental thermal conductivity values for HB-40 or Hydrogenated Santowax OM are available in the literature³ to enable a comparison with the absolute values determined in this work.

TABLE IEXPERIMENTAL VALUES OF THE THERMAL CONDUCTIVITY OF CARBON
TETRACHLORIDE

Test Temperature °F	Thermal Conductivity of the Liquid Btu/(Hr)(Ft)(°F)
69.25	0.0692
87.64	0.0821
100.57	0.0892
124.94	0.0825
150.40	0.0880
168.41	0.0856

GRAPH NO. I

THERMAL CONDUCTIVITY OF CARBON TETRACHLORIDE

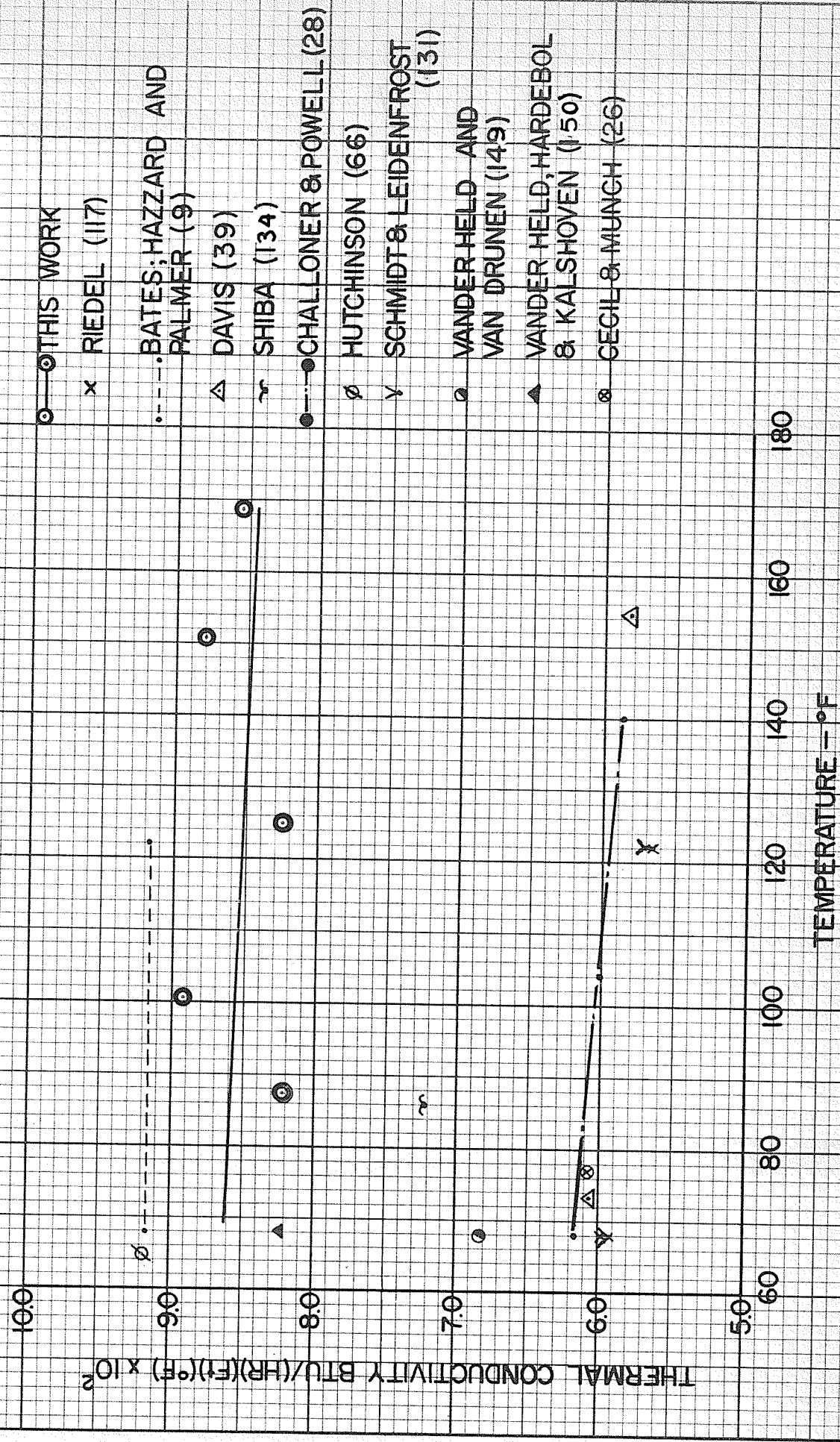


TABLE 2EXPERIMENTAL VALUES OF THE THERMAL CONDUCTIVITY OF TOLUENE

Test Temperature °F	Thermal Conductivity of the Liquid Btu/(Hr)(Ft)(°F)
69.89	0.0723
86.98	0.0777
99.09	0.0769
123.37	0.0773
149.76	0.0795
167.58	0.0792
195.05	0.0823
216.91	0.0901
230.12	0.0895

GRAPH NO. 2

THERMAL CONDUCTIVITY OF TOLUENE

- THIS WORK
- CHALLONER AND POWELL (28)
- x RIEDEL (117)
- WEBER AND JAKOB (157)(69)
- ABAS-ZADE (2)
- ∅ KARDOS (74)
- BRIDGEMAN (23)
- ▲ SMITH (135)
- ⊗ ZIEBLAND (163)
- ∨ SCHMIDT AND LEIDENFROST (131)
- ~ SHIBA (134)
- △ DAVIS (39)

THERMAL CONDUCTIVITY BTU/(HR)(F)² × 10²

TEMPERATURE - °F



TABLE 3EXPERIMENTAL VALUES OF THE THERMAL CONDUCTIVITY OF HB-40

Test Temperature °F	Thermal Conductivity of the Liquid Btu/(Hr)(Ft)(°F)
250.16	0.0545
300.33	0.0611
350.33	0.0680
401.76	0.0723
451.06	0.0805
500.29	0.0885
551.20	0.0978
603.21	0.1177

GRAPH NO. 3
THERMAL CONDUCTIVITY OF HB - 40

THERMAL CONDUCTIVITY $\times 10^2$ BTU/(HR)(F) (°F)

TEMPERATURE - °F

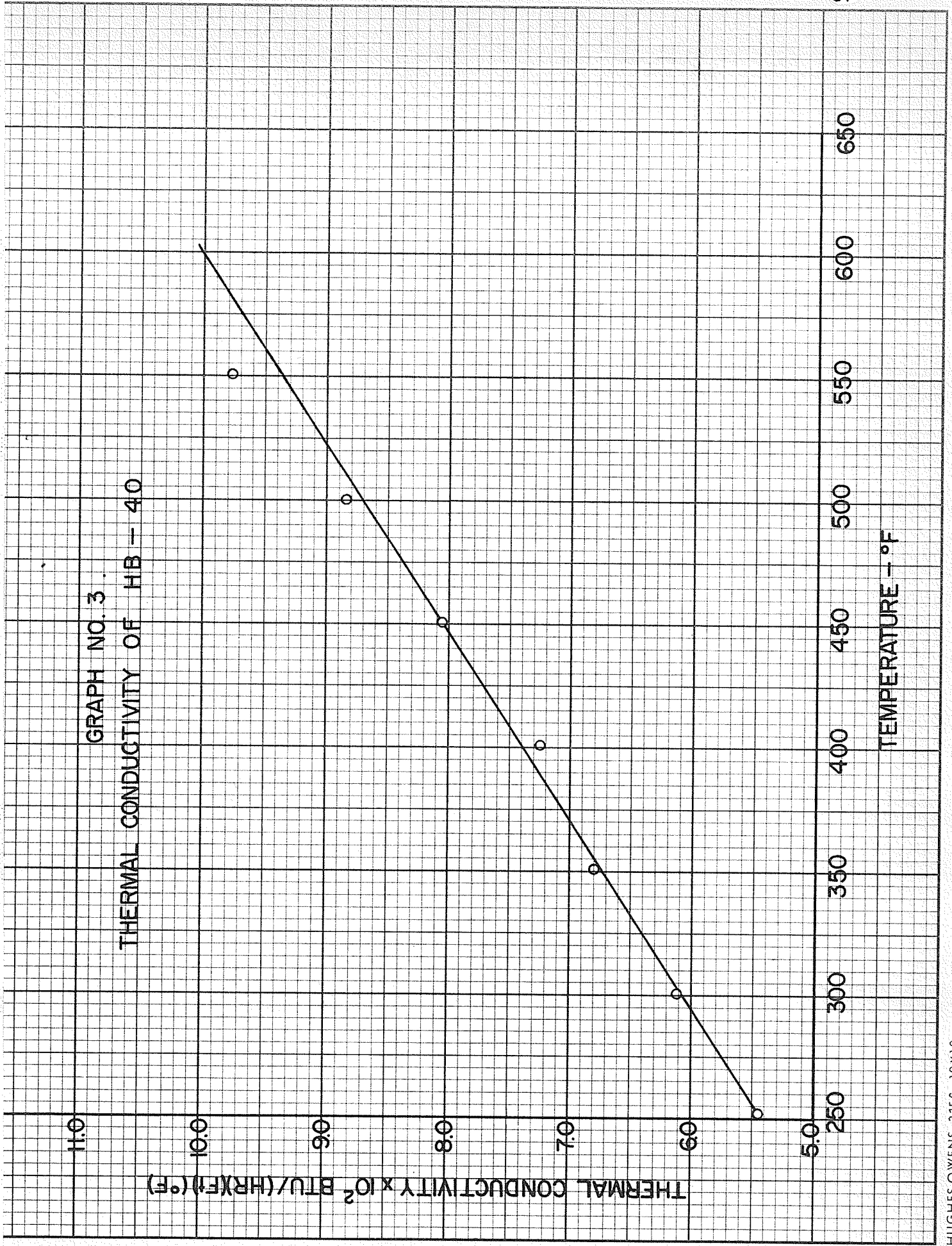


TABLE 4

EXPERIMENTAL VALUES OF THE THERMAL CONDUCTIVITY OF HYDRO-
GENATED SANTOWAX OM

Test Temperature OF	Thermal Conductivity of the Liquid Btu/(Hr)(Ft)(°F)
251.44	0.0580
302.30	0.0603
354.55	0.0638
400.07	0.0661
449.64	0.0683
499.39	0.0713
549.49	0.0751
599.86	0.0823

GRAPH NO. 4

THERMAL CONDUCTIVITY OF HYDROGENATED SANTOWAX OM

THERMAL CONDUCTIVITY $\times 10^2$ BTU/(HR)(F²)(°F)

5.0

6.0

7.0

8.0

9.0

250

300

350

400

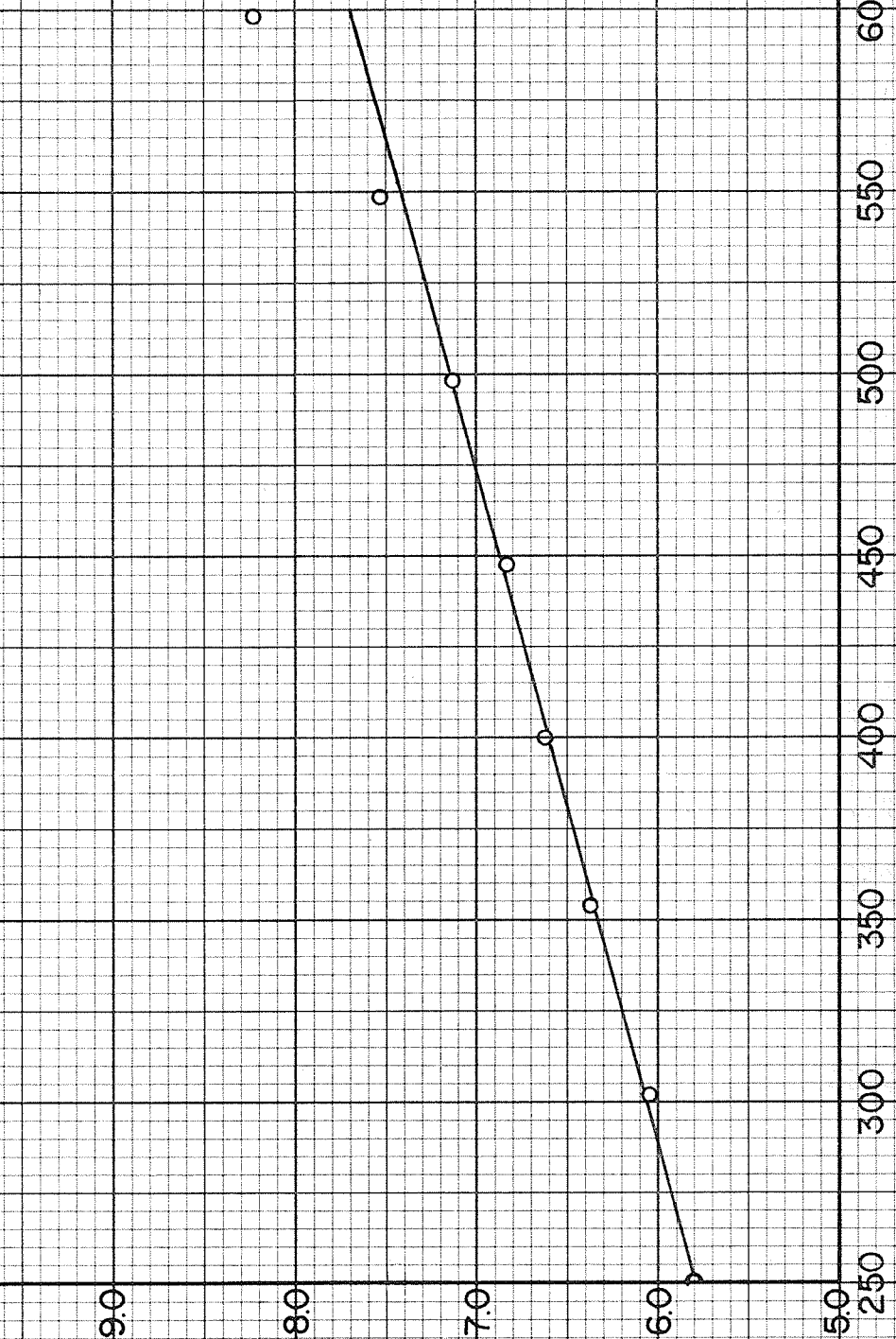
450

500

550

600

TEMPERATURE - °F



IX : DISCUSSION OF RESULTS AND CONCLUSIONS

The hot-wire cell as designed and constructed has been used successfully to measure the absolute thermal conductivity of organic liquids from room temperature to 600°F. The cell has considerable flexibility; the temperature difference across the liquid film can be varied and the liquid can be pressurised to about 100 psi., without damaging the cell. It has been suggested⁵⁴ that for the thermal conductivity to be sufficiently accurate, the constant temperature bath containing the cells must be controlled to at least $\pm 0.005^\circ\text{F}$. This condition was adequately met in the present work as the bath used was controlled to $\pm 0.002^\circ\text{F}$ over the complete test temperature range. This accuracy of temperature control was maintained for all test periods, which in some cases lasted over an hour.

The reproducibility and precision of the equipment was checked by making three runs each with Carbon Tetrachloride and Toluene, and, two runs each with organic coolants, HB-40 and Hydrogenated Santowax OM. The thermal conductivities at test temperatures of each liquid for every run were calculated, and the resulting values did not vary by more than $\pm 2\%$ for the total number of test runs completed with each liquid.

The accuracy of the determination made with the equipment may be estimated by taking into consideration the errors in the measurement of each quantity entering the heat-conduction equation. The electrical power supplied to the test section was determined by measuring the voltage drop across a precision resistor placed in series with the test

section. The voltage drop was measured with the precision potentiometer to an accuracy of 0.01% and the shunt resistance was measured on a precision Kelvin bridge to 0.01%. The electrical current supplied to the cell was thus calculated to an accuracy of 0.02%. The resistance of the test section filament, when dissipating heat at steady state, was measured to 0.002% of its resistance over the complete range. To calculate the thermal conductivity values of the liquids tested, the mean radius of the test section filament was employed and an estimated error in accuracy of $\pm 2\%$ was introduced by this procedure. The relatively large error of $\pm 2\%$ in measuring the test section filament radius was mainly due to the "spring back" of the filament after the removal of the winding core. An error of $\pm 1.5\%$ was also introduced by uncertainties in length and thus an overall error of $\pm 3.5\%$ by the geometry of the cell. The outside diameter of the glass tube containing the test section filament was measured to an accuracy of 0.01%. The bore of this glass tube was stated by the Chemistry Department, who assembled the cell, to be accurate to within 0.1%. The temperature difference across the liquid layer was calculated from the pre-tests calibrations to an accuracy of 0.2%. This temperature difference was assumed to exist between the "emitting cylinder" represented by the mean diameter of the test section filament and the "receiving cylinder" represented by the inside diameter of the glass tube containing the test section. If, however, the measured temperature difference is in fact between the cylinders represented by the outside diameter of the filament and the bore of the glass tube containing the filament, then the error in

assuming that the mean diameter of the filament is in effect the temperature of the "emitting cylinder" can be calculated by employing the "buried cable" theory or a flux plot. By using these methods the error in the calculated thermal conductivity values was approximated to 2.4%. Taking into account all errors discussed above, the maximum possible error in the measurements of the quantities entering the heat conduction equation was therefore of the order of $\pm 7\%$ but the probable error is estimated to be of the order of $\pm 5\%$. The difference being due to the method used in allowing for the discrepancy of the geometry.

While assembling the cell, great care was taken in centralizing the filaments in their respective glass tubes. In the assessment of possible errors and in the calculations of the thermal conductivity of the liquids tested, perfect concentricity has been assumed. It is apparent that a further error will exist in the calculations if the filaments are not located concentrically. The magnitude of the error thus introduced will depend on the eccentricity of the filaments.

The equation (VII.4) was used to calculate all thermal conductivity values obtained in this work with the hot-wire cell. For the equation to hold there should be no significant temperature difference between the outer wall of the glass tube and the bath liquid. If a temperature gradient exists on the outer wall then an error will exist in the values calculated by using equation (VII.4). The magnitude of the error introduced by this film temperature drop, if existent, will depend upon the convective coefficient and the agitation of the bath.

Apart from the errors introduced by inaccurate measurements of the various quantities entering the heat conduction equation, the accuracy of results depends entirely on establishing equilibrium conditions during the tests. The procedure followed to ensure that equilibrium conditions prevailed during all tests has been explained fully in part VI of the thesis. This procedure can briefly be summarized as below.

- (1) The bath was heated to the desired temperature and its temperature controlled to $\pm 0.002^{\circ}\text{F}$ by the method outlined in part VI.
- (2) The resistance of the test section filament was measured accurately and its temperature determined from the pre-tests calibrations. In all cases the temperature of the filament was equal to the temperature of the bath.
- (3) The bath temperature was controlled to $\pm 0.002^{\circ}\text{F}$ for at least one hour prior to passing the heating current through the filaments.
- (4) The resistance of the test section filament was continuously measured when the heating current was passing through it. When this resistance did not vary for fifteen to twenty minutes, the filament was assumed to be transferring heat at steady state.
- (5) When the heating current was passing through the test section filaments, the adjustable thermocouple probes were always in contact with the outside of the glass tube

containing the test section filament. This precaution was taken to detect any temperature difference between the outer wall of the glass tube and the bath medium.

- (6) At the completion of the test, the bath temperature was re-checked by using the resistance thermometer and the adjustable thermocouple probes. If the bath temperature had varied by more than $\pm 0.002^{\circ}\text{F}$ from the temperature at the beginning of the test, the data for the test was rejected.

The hot-wire cell was originally designed for the measurements of the thermal conductivity of viscous organic coolants. A number of workers^{26,27,66,156,157} have employed a similar cell to obtain thermal conductivity values. Before testing HE-40 and Hydrogenated Santowax OM, it was decided to test Carbon Tetrachloride and Toluene, and compare the experimental values thus obtained with the most reliable values in the literature.

In view of the experimental difficulties it is not surprising that the results of different authors for the thermal conductivity of the same substance have not always been in good agreement. A large discrepancy, for instance, exists in the data for Carbon Tetrachloride and Toluene, obtained by various workers over a number of years. Graph No. 1 and Graph No. 2 show the experimental absolute thermal conductivity values obtained in this research for Carbon Tetrachloride and Toluene respectively. A comparison of the values obtained for the above mentioned two liquids is made with the data of other workers which has been

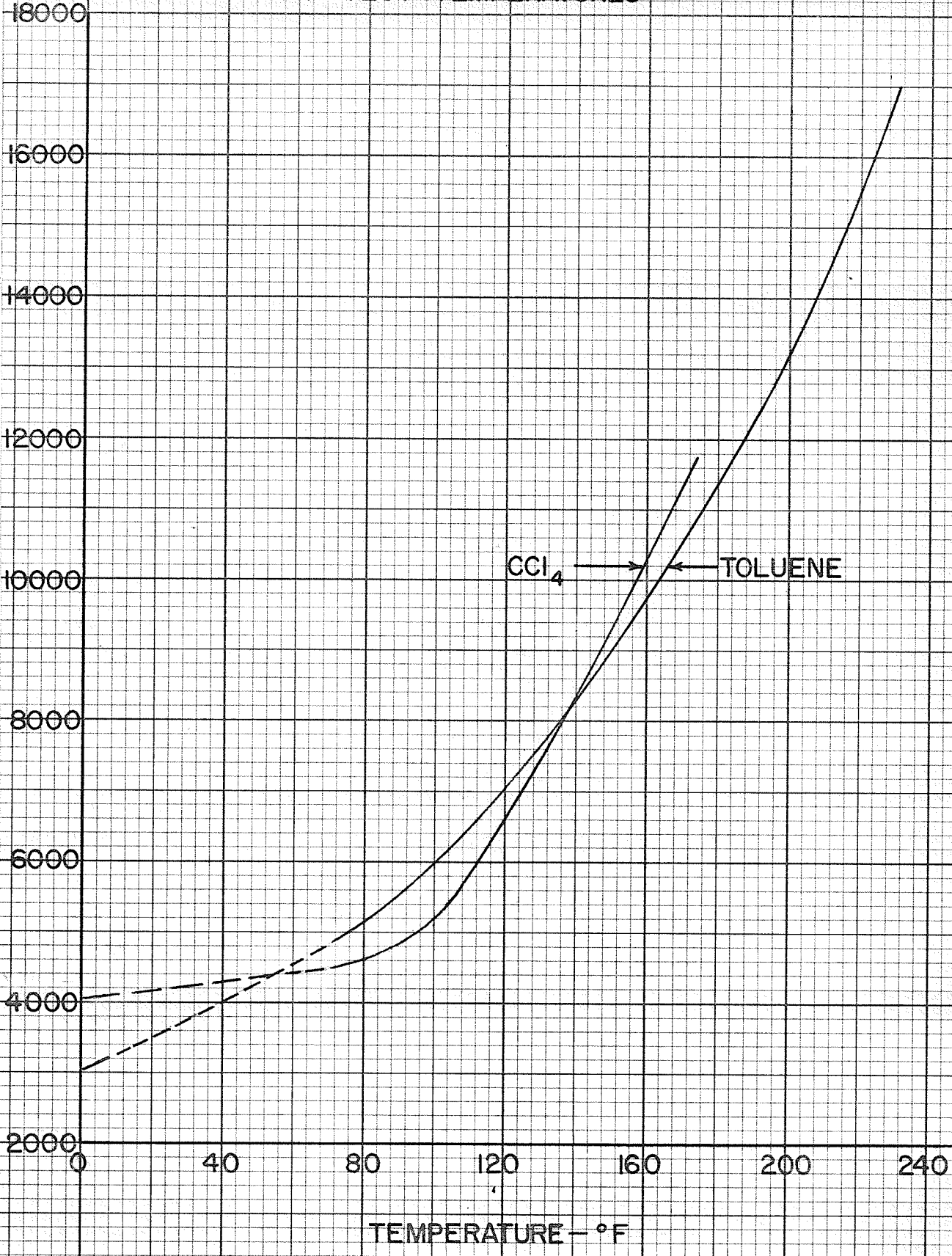
frequently quoted in the relevant literature. It was indeed fortunate that most of the determinations were absolute ones and were made with different types of conductivity cells employing different methods of temperature measurements. Greater confidence can obviously be put into average values which were derived from an analysis of data obtained by different methods, as the possibility of propagating inherent errors due to the use of only one experimental method is eliminated.

Graph No. 1, contains the absolute values obtained for samples of Carbon Tetrachloride when tested in the hot-wire cell. The "reliable" values obtained by other workers are included in this graph and some surprisingly large deviations are apparent. The values obtained during the course of the present work are considerably higher than those obtained by Challoner and Powell²⁸, Davis³⁹, Riedel¹¹⁷, Schmidt and Leidenfrost¹³¹, and, Shiba¹³⁴, but lower than those obtained by Hutchinson⁶⁶, and, Bates, Hazzard and Palmer¹⁰. There is a good agreement between the values obtained by Challoner and Powell²⁸, Davis³⁹, Riedel¹¹⁷, Schmidt and Leidenfrost¹³¹ and these values are among the best available. The results of these authors' work are further supported by the extensive series of measurements carried out by Filipov, using different designs of thin-film, steady-state cells⁴⁸.

After the first test run on Carbon Tetrachloride was completed, the thermal conductivity values were calculated. It was seen that these values were considerably higher than the accepted values of Challoner and Powell²⁸, Riedel¹¹⁷ and Schmidt and Leidenfrost¹³¹. Two more test runs were made to see if any errors existed in the test

procedure. When the results of all the runs at each temperature were reproducible to within $\pm 2\%$, the possibility of convection in the cell was investigated. Approximate values of the product of Grashof and Prandtl numbers, $(N_{GR})(N_{PR})$, for Carbon Tetrachloride at the test temperatures were calculated by using the average temperature differences obtained during the tests. These values are shown in Table 6 and are plotted on Graph No. 5 shown on the next page. It is seen that $(N_{GR})(N_{PR})$ product increases slowly to about 96°F and then rises sharply. However if the graph is extrapolated back to 0°F , it is noticed that the $(N_{GR})(N_{PR})$ product for the cell is about 4000, which is considerably higher than the upper limit of 1000^{146} if convection is to be insignificant. This criterion points out, therefore, that at all the test temperatures for Carbon Tetrachloride, heat was not transferred by pure conduction only. The scatter in the data obtained indicates that 'cellular motion' was present in the cell at all test temperatures. The experimental values further indicate that the 'cellular motion' was not fully developed and broke down due to insufficient thermal energy being supplied to the cell. A value of the thermal conductivity of Carbon Tetrachloride was measured at 69.25°F , and although this value agrees with that of Van der Held and Van Drunen¹⁴⁹, it was rejected because of the difficulty in controlling the bath temperature to the desired accuracy at room temperature. The present cell, therefore, is unsuitable for accurate determination of the absolute thermal conductivity values of Carbon Tetrachloride. It is felt that the large discrepancy between the data of various workers for Carbon Tetra-

ESTIMATED $N_{GR} \cdot N_{PR}$ PRODUCT
FOR TOLUENE AND CARBON TETRACHLORIDE
AT TEST TEMPERATURES



chloride is due largely to convection in their cells. Hutchinson⁶⁶, for instance, used a hot-wire cell similar to the one used for this work, and his data has been criticized²⁸ on account of convection.

Cecil and Munch²⁶ also employed a hot-wire cell similar to the one used for this research, and they checked for convection by measuring the thermal conductivity of an approximate 2.5% solution of gelatin in distilled water. Although the viscosity of this solution was six times that of water, its thermal conductivity was found to be equal to that of distilled water. The authors omitted to state the temperature at which they performed this test, however they did state their value for the thermal conductivity of Carbon Tetrachloride at 77°F, which a comparison showed was less than the value stated by Challoner and Powell²⁸, but was higher than the values determined by Riedel¹¹⁷, and, Schmidt and Leidenfrost¹³¹. The rejected test made on Carbon Tetrachloride at 69.25°F yielded a thermal conductivity value which was only 10% higher than that of Challoner and Powell²⁸. Therefore it appears as if Cecil and Munch²⁶ tested Carbon Tetrachloride at higher temperatures than 77°, in which case convection would have been set up in their cell, as was the case in the hot-wire cell used in this study.

The experimental thermal conductivity values for Toluene are contained in Graph No. 2. As in the case of Carbon Tetrachloride, the "reliable" values for Toluene, obtained by other investigators, are included on this graph, and again large deviations are noticed. At the first look, it is noticed that the values determined in this research agree well with the values of others up to 168°F. On closer examination

it is seen, however, that Challoner and Powell²⁸, Riedel¹¹⁷, Schmidt and Leidenfrost¹³¹, and, Ziebland¹⁶³ found that the thermal conductivity of Toluene decreases with increasing temperature, as indeed is the case for most liquids. The values of this research between 86°F and 100°F do decrease with increasing temperature and then begin to increase with increasing temperature. A line through the values of Challoner and Powell²⁸ passes through the values obtained in this work at 86°F and 100°F. Since there is excellent agreement between the values of Challoner and Powell²⁸, Riedel¹¹⁷, Schmidt and Leidenfrost¹³¹, and Ziebland¹⁶³, the accuracy of the values obtained here up to 100°F can be accepted. Although the thermal conductivity of Toluene was determined at room temperature, it is not shown on Graph No. 2 as it is thought to be inaccurate due to the difficulty in controlling the bath temperature at room temperature.

When the thermal conductivity started to increase after about 100°F, the possibility of convection in the cell was again investigated. Approximate values of $(N_{GR})(N_{PR})$ product at the test temperatures were calculated by using the actual temperature differences obtained during the tests. These values are shown in Table 7 and are plotted on Graph No. 5. When the graph is extrapolated back to 0°F, the $(N_{GR})(N_{PR})$ product is about 3000 which is considerably higher than the upper limit of 1000¹⁴⁶. The results of this research seem to indicate, however, that if there is convection in the cell it is insignificant till about 100°F. At 100°F, the $(N_{GR})(N_{PR})$ product is about 6000, which definitely points to the presence of convection.

However these results are acceptable for Toluene at temperatures up to 100°F but after that the results of Challoner and Powell²⁸, Riedel¹¹⁷, Schmidt and Leidenfrost¹³¹, and Ziebland¹⁶³ should be used.

In order to check the reproducibility of results three separate test runs were taken with Toluene. The results of all three runs at each temperature were reproducible to within $\pm 2\%$. The scatter in results indicates that although convection was present at all test temperatures and had a marked effect on the results after 100°F, the 'cellular motion' was again not fully developed and broke down due to insufficient thermal energy being supplied to the cell.

As shown on Graph No. 2, the values of Abas-Zade², Bridgman²³, Davis³⁹, Kardos⁷⁴, Shiba¹³⁴ and Smith¹³⁵ agree well, they are consistently higher than those of Challoner and Powell²⁸, Riedel¹¹⁷, Schmidt and Leidenfrost¹³¹, Ziebland¹⁶³, and this work, and, should not, therefore, be used for any accurate applications. The values of Weber¹⁵⁷ and Jakob⁶⁹ are not in agreement with those determined later by other authors, and can be regarded as being the least accurate of all available data. Smith¹³⁵ reproduced the values obtained by Bridgman²³ but he used the concentric cylinder cell of Bridgman. There is however, a close agreement between the values of Bridgman and Abas-Zade² for Toluene determined with co-axial cylinders and hot-wire cells respectively. The causes which may have led to the relatively large discrepancies between Bridgman's determination and

those of later workers have been thoroughly discussed by Riedel¹¹⁷ and need not be repeated here. From the close agreement between the work of Abas-Zade and Bridgman, one could almost gain the impression that the former author's apparatus was calibrated with the aid of Bridgman's results.

The Atomic Energy of Canada Limited³, (A.E.C.L.), and other industrial groups in Canada engaged in various aspects of nuclear energy, have expressed interest in obtaining original thermal conductivity data on organic coolants. A.E.C.L. have specified Hydrogenated Santowax OM as one of the possible coolants for use in the new Whiteshell Reactor, and HB-40 is planned to be used in the fuel washing systems at the same reactor site. HB-40 is Santowax OMP hydrogenated to 40% of the maximum theoretical amount. Samples of these coolants were obtained from A.E.C.L. and their thermal conductivity values determined experimentally between 250°F and 600°F.

The resulting values are shown on Graph Nos. 3 and 4. Previous experimental data had not been published³ on these organics and, therefore, no comparisons with the values obtained in this work were made. The thermal conductivity values obtained during the course of this research increase with increasing temperatures as indicated on the appropriate graphs.

In order to check for convection in the cell at test temperatures the values for the product of Grashof and Prandtl numbers, $(N_{GR})(N_{PR})$, for both organics at each test temperature were estimated. When searching for suitable property values to evaluate the Rayleigh

modulus, it was noticed that the viscosity of organic reactor coolants^{6,43} decreases rapidly as the temperature increases. The estimated values of the Rayleigh modulus for both organics at each test temperature are shown in Tables 8 and 9. Taking the critical value of the Rayleigh modulus as 1000^{146} , convection was present during all tests for Hydrogenated Santowax OM and, therefore, the thermal conductivity values are unreliable. However, the values of the Rayleigh modulus were below 1000 for the HB-40 tests at 250 and 300°F. In reference 6, the thermal conductivity of HB-40 at 200°F is stated to be 0.065 Btu/(Hr)(Ft)(°F) which indicates that the values obtained in this research for the same liquid at 250 and 300°F are far too low.

As stated earlier equation (VII.4) was used to calculate all thermal conductivity values and the equation assumes that there is no significant temperature difference between the outer wall of the glass tube containing the test section filament and the bath medium. During the course of each test, the two adjustable thermocouple probes were always in contact with the outside of the glass tube containing the test section filament. These thermocouples could only measure the temperature accurately to 0.3°F. Since the average temperature drop across the test liquid layer was in the order of 1°F, a considerable error in the measured thermal conductivity values could exist due to neglecting the film temperature drop, if existent, on the outside of the glass tube. No temperature difference between the outside of the glass tube containing the test section filament and the bath medium was detected during the course of the reported work and consequently

no correction was made for any film temperature drop on the outside of the glass tube. A correction for the error due to a temperature drop on the outer surface of the glass would reduce the effective temperature drop across the test layer and thus increase the value of K.

Each complete test with the organics was performed without any shut downs and both coolants were continuously subjected to temperatures above 300°F for at least thirty five hours. It was noticed that the coolants started to discolour after a few hours use at temperatures above 300°F and it was then thought that perhaps the coolants started to breakdown. A subsequent check with people associated with the organics pointed out that decomposition was not possible with the limited heating encountered. Thus the discolouration could have been caused by a leakage of the bath medium into the cell or by any impurities that might have been present in the tungsten wire used in the manufacture of the filaments. In this case an oxide film could have been deposited on the surfaces of the filaments which would introduce an extra resistance to the heat flow from the test section filament. Therefore less heat than that calculated by measuring the resistance of the test section would be conducted through the layer and low thermal conductivity values would result as in the case of HB-40 at 250 and 300°F. The resistance of the filament should have been checked after the tests.

It has been observed in the evaluation of the empirical correlations and theoretical equations that the groups of physical properties involved do not account for variations in the observed

thermal conductivity. As the study showed no one equation predicts the thermal conductivity value for all liquids and, therefore, experimental data should be used if available.

The experimental results have shown that the hot-wire cell used in this study is only suitable for measuring the absolute thermal conductivity values of viscous liquids. If it is desired to use a hot-wire cell at elevated temperatures to measure the thermal conductivity of low viscosity liquids, then a modified cell similar in design to that used for the reported work may be employed. To minimize convection in the cell, however, it will be advisable to reduce the present film thickness.

The construction of a hot-wire cell requires a good craftsman. Several authors have remarked on their difficulty in centering the heated wire with the required precision in the surrounding glass tube. This difficulty eventually forced them to resort to some form of calibration with a liquid of "known" thermal conductivity for determining the true geometrical constants for their cells.

All the quantities required for the calculation of the cell geometric constants can be measured precisely. Some controversy existed over the radius of the coiled filament to be used in the calculations of the cell constant. The filament was closely wound on a solid core, which was removed before assembly, and the coil experienced "spring back". For the results stated in this report, the mean diameter of the filament was used. When assembling the apparatus, great care should be taken to avoid heat flow down the glass tube as

this heat flow could distort the tube thus resulting in a non-uniform film thickness. Despite all the assembly difficulties an accurate cell was constructed and thermal conductivity values determined for two new organic coolants.

It is sincerely hoped that the performance of the hot-wire cell will be checked with the concentric cylinder cell when it is completed. The accuracy and precision of the concentric cylinder cell should be checked by taking a few test runs with Carbon Tetrachloride and Toluene, and by comparing the values obtained with those recommended in this report. Once the accuracy of the concentric cylinder cell has been established, it should be a relatively easy matter to carry out measurements at higher temperatures and pressures.

The most important auxiliary equipment, namely the constant temperature bath, has proved to be a highly suitable piece of equipment and can be controlled to the limit specified earlier, over a long period of time. Cooling coils or a thermo-electric cooler should be installed in the bath, however, to enable tests at temperatures below the room temperature. Additional heating coils, wrapped on the outside of the bath, will help to heat the viscous tempering oil, which is necessary for temperatures above 230°F. The techniques for carrying out the tests have been well established and the future users of the equipment should have no difficulties if the precautions outlined in the report are exercised.

X : BIBLIOGRAPHY AND REFERENCES

1. Abas-Zade, A.K., "Measurements of the Heat Conductivity of Liquids and Vapors at High Temperatures and Pressures". Dokaldy Akad. Nauk Azaebaidzhan, USSR, 3, No. 1 : 2; 1947.
- 2.(a) Abas-Zade, A.K., "Investigation of the Thermal Conductivity of Some Organic Compounds in the Critical Region". Dokl. Akad. Nauk, USSR, 68 (No. 4) : 665; 1949.
- 2.(b) Abas-Zade, A.K., J. Exp. Theor. Phys., 23, 60; 1952.
3. Aikin, A.M., Chemistry and Metallurgy Division, Atomic Energy of Canada Ltd., Chalk River, Ont. Private Communications, Oct. 1962.
4. Allen, P.H.G., "Fluid Thermal Conductivity by a Transient Method". Symposium on Thermal Properties. Heat Transfer Div., ASME., 350; 1959.
5. American Institute of Physics, "Temperature, Its Measurement and Control in Science and Industry". Reinhold Publishing Corporation, New York, Vols. I and II; 1941 and 1955.
6. Atomic Energy of Canada Limited, "OTR Designer's Manual of Organic Coolant Properties". Report No. CE 1-142; Feb. 1962.
7. Bates, K.O., "Thermal Conductivity of Liquids", Ind. Eng. Chem., 25 : 431; 1933.
8. Bates, K.O., "Binary Mixtures of Water and Glycerol". Ind. Eng. Chem., 28 : 494; 1936.
9. Bates, K.O.; Hazzard G.; and Palmer, G., "Thermal Conductivity of Liquids, Binary Mixtures of Water-Methyle Alcohol, and Water-Ethyl Alcohol". Ind. Eng. Chem., 10 : 314; 1938.
10. Bates, K.O.; Hazzard, G.; and Palmer, G., "Thermal Conductivity of Liquids. Twelve Chlorinated Hydrocarbons". Ind. Eng., Chem., 33 : 375; 1941.
11. Bates, K.O.; and Hazzard, G., "Thermal Conductivity of Alcohols and Glycols". Ind. Eng. Chem., 37 : 193; 1945.
12. Bates, K.O., "Thermal Conductivity of Liquid Silicones". Ind. Eng. Chem., 41 : 1966; 1949.
13. Bearman, R.J., J. Chem. Phys. 6 : 833; 1958.
14. Bearman, R.J., and Kirkwood, J.G., J. Chem. Phys. 28 : 136; 1958.

15. Beck, J.V.; and Hurwicz, J., "Effect of Thermocouple Gravity on Heat Sink Temperature". Trans. A.S.M.E., J. of Heat Trans. 82 : Series C ; 27;1960.
16. Becker, J.A.; Green, C.B.; and Pearson, G.L., "Properties and Uses of Thermistors - Thermally Sensitive Resistors". Trans. A.I.E.E., 65 : 711;1946.
17. Beckmann, W., Forschungsh. Ver. Dtsch. Ing., 2 : 213;1931.
18. Bennowitz, K.; and Rossner, W.Z., Phys. Che., B. 39 : 126;1938.
19. Bird, R.B.; Steward, W.E.; and Lightfoot, E.N., "Transport Phenomena". John Wiley and Sons, Inc., New York, 1960.
20. Bondi, A.J., J. Chem. Phys. ; 19 : 28 ; 1951.
21. Bottomley, Proc. Roy. Soc., 28 : 462;1879. 31 : 300;1881. Phil. Trans., 172 : 537;1881.
22. Born, M.; and Green, H.S.; Proc. Roy. Soc. A 190 : 455;1947.
23. Bridgman, P.W., "The Thermal Conductivity of Liquids under Pressure". Am. Acad. Arts and Sci., 49 : 141;1923.
24. Briggs, D.K.H., "Thermal Conductivity of Liquids". Ind. Eng. Chem. 49 : No. 12; 418;1957.
25. Carslaw, H.S.; and Jaeger, J.C., "Conduction of Heat in Solids". Oxford University Press, London. 1947.
26. Cecil, O.B.; and Munch, R.H., "Thermal Conductivity of Some Organic Liquids". Ind. Eng. Chem., 48 : 437;1956.
27. Cecil, O.B. ; Koerner, W.E. ; Munch, R.H., "Thermal Conductivity of Some Organic Liquids - High Temperature Measurements". Ind. Eng. Chem., 2 : 54;1957.
28. Challoner, A.R. ; and Powell, R.W., "Thermal Conductivity of Liquids : New Determinations for Seven Liquids and Appraisal of Existing Values". Proc. Roy. Soc., A 238 : 90;1956.
29. Challoner, A.R. ; and Powell, R.W., "A Radial Heat-Flow Apparatus for Liquid Thermal Conductivity Determinations". Proc. Roy. Soc. A 245 : 259;1958.
30. Chree, C., Proc. Roy. Soc., 43 : 30;1888.
31. Christiansen, Ann. Phys., 14 : 23;1881.

32. Classon, T.W.; and Nelidoff, J., Phys. Z. Sowjet, 5 : 191;1934.
33. Corning Glass Works, Corning, New York. "Properties of Selected Commercial Glasses". Bull. B 83.
34. Corning Glass Works, Corning, New York. "Thermal Conductivity of Pyrex Brand Glass No. 7740". Private Communication. Feb.1963.
35. Cragoe, C.S., "Thermal Conductivity of Petroleum Liquids". U. S. Dept. of Comm., Bureau of Standards ; Misc. Pub. 97.
36. Crow, L.R., "Saturating Core Devices". Scientific Book Publishing Company, Vincennes, Ind. 1956.
37. Dalton, Manch. Mem., 5, ii : 373;1802.
38. Daniloff, M., "The thermal Conductivity of the Normal Primary Saturated Alcohols". J. Am. Chem. Soc., 54 : 1328;1932.
39. Davis, H.A., "Some Thermal Conductivity Data". Phil. Mag., 47 : 972;1924.
40. Debye, P., Vortrage uber der kinetischen theorie der Materie und Elektrizitat. Teubner, Berlin, 1914. Quoted by L.S.Kowalczyck, Trans. A.S.M.E. 77 : 1021;1955.
41. Despretz, Compt. Rend., 7 : 933;1838.
Ann. chim., 71 : 206;1838.
Ann. Phys., 142 : 417;1871.
42. Dick, M.F.; and McCready, D.W., "The Thermal Conductivity of Some Organic Liquids". Trans. A.S.M.E., 76 : 3021;1954.
43. Dowtherm Handbook, The Dow Chemical Company, Midland, Michigan.
44. Eckert, E.R.G.; and Drake, R.M., "Heat and Mass Transfer". McGraw-Hill Book Co., Inc., New York 36, N.Y. 1959.
45. Erk, S.; and Keller, A., "The Thermal Conductivity of Glycerol - Water Mixtures". Phys. Zeit., 37 : 353;1936.
46. Eucken, A.; and Englert, H., Z. ges. Kalteind, 45 : 109;1938.
47. Ettlinger, G.M., "Magnetic Amplifiers". John Wiley and Sons, Inc., New York. 1953.
48. Filippov, L.P., Vestn. Mosk. Univ. ; No. 9 : 109;1953.
No. 6 : 56;1954.
No. 12 : 45;1954.
No. 8 : 67;1955.

49. Filippov, L.P.; and Novoselova, N.S., Vestn. Mosk. Univ., No. 3 : 37;1955.
50. Fourier, J.B.J., "Theorie analytique de la chaleur". Gauthier-Villars, Paris, 1822. English translation by Freeman, Cambridge, 1878.
51. Fournier, A.C.R., Acad. Sci., Paris; 221 : 294;1945.
52. Frontasev, V.P., Zhur. Fiz. Khim., 20 : 91;1946.
53. Frontasev, V.P.; and Gusakov, M.Ya., "The Heat Conductivity of Certain Organic Liquids". Soviet Phys. - Tech. Phys., 4(10) : 1171;1960.
54. Gercke, R.H.J., Atomics International, Canoga Park, Cali. Private Communication, Jan. 1962.
55. Gillam, D.G.; Romben, L.; Nissen, H.E.; and Lamm, O., "Accurate Determination of Thermal Conductivities". Acta Chem. Scand. 9 : 641;1955.
56. Gillam, D.G.; and Lamm, O., "Precision Measurement of the Thermal Conductivity of Certain Liquids using the Hot Wire Method", Acta Chem. Scand., 9 : 657;1955.
57. Goldschmidt, Phys. Z., 12 : 417;1911.
58. Goodyear, R.S., "Thermistors - Descriptions, Applications, and Stability Data". Fenwal Electronics, Inc. Framingham, Mass. Sept. 1961.
59. Graetz, L., Ann. Phys., 18 : 79;1883. 25 : 337;1885.
60. Guthrie, G., Phil. Mag., 35 : 283;1868; 37 : 468;1869. Phil. Trans., 159 : 637;1869.
61. Hager, N.E. Jr., "Thin Heater Thermal Conductivity Apparatus". Rev. Sci. Inst., No. 2, 31 : 177;1960.
62. Hammann, G., "Thermal Conductivity of Liquid Oxygen, Liquid Nitrogen and their Mixtures". Ann. Phys., Series 5, 32 : 593; 1938.
63. Haupin, W.E., "Hot Wire Method for Rapid Determination of Thermal Conductivity". Am. Ceram. Soc. Bull., 39 : 139;1960.
64. Hertz, I.G. ; and Filippov, L.P., Zhur. Fiz. Khim., 30 : 2424;1956.

65. Hickson, V.M., "The Welding of Thermocouple Junctions". J. Sci. Inst., 17 : 182;1940.
66. Hutchinson, E., "On The Measurement of the Thermal Conductivity of Liquids". Trans. Far. Soc., 41 : 87;1945.
67. "International Critical Tables" : Vol. 5 : p. 226 : McGraw-Hill Book Company, New York. 1929.
68. Jager, Wien Ber., 99, II : 245;1890.
69. Jakob, M., Ann. Phys., 63 : 537 (bibl) ; 1920.
70. Jakob, M., "Heat Transfer", Vol I, II. John Wiley and Sons, New York. 1949.
71. Jeffreys, H., Proc. Roy. Soc., A 118 : 195;1928.
72. Johanin, P. ; and Vodar, B., "Thermal Conductivity of Nitrogen at High Temperatures and Pressures". Ind. Eng., Chem. No. 12 : 49 : 2040;1957.
73. Kallan, F.L., "The Thermal Conductivity of Liquids". Mech. Engr. 45 : 479;1923.
74. Kardos, A., "A Measurement of Thermal Conductivity of Different Liquids". Zeit, V.D.I., 77 : 1158;1933.
75. Kaye, G.W.C. ; and Higgins, W.F., "Thermal Conductivity of Certain Liquids". Proc. Roy. Soc., A 117 : 459;1927-28.
76. Kaye, G.W.C. ; and Higgins, W.F., "Thermal Conductivity of Solid and Liquid Sulphur". Proc. Roy. Soc. A. 122 : 633;1929.
77. Kern, D.Q. ; and Nostrand, W.V., "Heat Transfer Characteristics of Fatty Acids". Ind. Eng. Chem., 41 : 2209;1949.
78. Kincaid, J.F. ; and Eyring, H.J., J. Chem. Phys., 6 : 620;1938 ;
79. Kowalczyk, L.S., "Thermal Conductivity and its Variability with Temperature and Pressure". Trans. A.S.M.E. 77 : 1021;1955.
80. Kraus, W., "Measurement of the Thermal Conductivity of Glycols". Z. Angen. Phys., 1 : 173;1948.
81. Kraussold, H., Forschungsh. Ver. Dtsch. Ing., 5 : 186;1934.
82. Lees, G.H., Phil. Trans., 191 : 399;1898.

83. Lilleleht, L.V., "An Apparatus for Measuring the Thermal Conductivities of Liquids". M.S. Thesis, Princeton University, 1955.
84. Lindemann, F.A., Phys. Z., 11 : 609;1910.
85. Linder, G.T., "The Measurement of Thermal Conductivity of Some Organic Liquids". M.S. Thesis, Louisiana State Univ., Baton Route, La., 1956.
86. Loeb, L.B., "Kinetic Theory of Gases". McGraw-Hill Book Company, New York, 1927.
87. Louis ; and Carrette, Chimie et Industrie, Spec. No. 556;1933, Ann. Combustibles Liquides, 8 : 133;1933.
88. Low, A.R., Proc. Roy. Soc. A 125;1929.
89. Markwood, W.H. ; and Benning, A.F., "Thermal Conductances and Heat Transmission Coefficients of Freon Refrigerants". Refr. Eng., 45 : 95;1943.
90. Martin, L.H. ; and Lang, K.C., "The Thermal Conductivity of Water" Proc. Phys. Soc., 45 : 523;1933.
91. McAdams, W.H., "Heat Transmission". McGraw-Hill Book Company, New York, 1954.
92. McNall, P.E. ; Woolf, J.R. ; Brock, J.E., "Methods for Controlling a Constant Temperature Bath". Proc. Indiana Acad. Sci., 301; 1950.
93. Mercury Commutator. Instruction Manual, Leeds and Northrup Company, Philadelphia, Pa.
94. Morris, R., Heat Div., Nat. Eng. Lab., Glasgow, Scotland, Private Communications, Feb. 1961.
95. Mueller Temperature Bridge. Instruction Manual, Leeds and Northrup Company, Philadelphia, Pa.
96. Mueller, E.F. ; and Wilhelm, R.M., "Methods of Testing Thermometers". Proc. A.S.T.M., 39 : Part I ; 493;1938.
97. Murray, J., Nicholson's J., 1 : 165, 241;1802.
98. National Research Council of Canada, "Calibration of Platinum Resistance Thermometer". Private Communication, Oct., 1962.
99. Pagerey, P.F. ; St. Clair, C.R. ; and Sibbitt, W.L., "The Thermal Conductivity of Organic Liquids". Trans. A.S.M.E., 78 : 1169;1956.

100. Palmer, G., "Thermal Conductivity of Liquids". Ind. Eng. Chem., 40 : 89;1948.
101. Parkins, S.R., "Experimental Determinations of the Thermal Conductivity of Liquids". M.S. Thesis, Purdue Univ., Lafayette, Ind. 1958.
102. Peierls, R., Ann. Phys. Lpz., 3 : 1055;1929.
103. Polissar, M.J., J. Chem. Phys., 6 : 833;1938.
104. Powell, R.E. ; Roweveare, W.E. ; Eyring, H., "Diffusion, Thermal Conductivity and Viscous Flow of Liquids". Ind. Eng. Chem., 33 : 430; 1941.
105. Precision Measurement and Calibration. Nat. Bureau Stands., Handbook 77 : Vol. II;1961.
106. Precision Potentiometer. Instruction Manual, Leeds and Northrup Company, Philadelphia, Pa.
107. Rao, M.R., "Thermal Conductivity of Liquids". Indian J. Phys., 16 : 161;1942.
108. Rayleigh, Lord. ; Phil. Mag., 32 : 529;1916.
109. Richter, G.N. ; and Sage, B.H., "Thermal Conductivity of Fluids". Ind. Eng. Chem., 4 : No. 12 ; 61;1957.
110. Riedel, L., "Measurement of Thermal Conductivity of Organic Liquids, Especially of Cooling Agents". Forschung, 340 : 1940.
111. Riedel, L., "Thermal Conductivity of Liquids". Mitt Kaltestech. Inst. Karlsruhe, No. 2, 45 pp.; 1947.
112. Riedel, L., "Measurement of the Thermal Conductivity of Liquids". Mitt Kaltestech Inst. Karlsruhe, 3 - 47 ; 1948.
113. Riedel, L., "Thermal Conductivity Measurements on Sugar Solutions, Fruit Juices and Milk". Chem. Ing. Tech., 21 : 340;1949.
114. Riedel, L., "Thermal Conductivity of Aqueous Sodium and Potassium Hydroxide Solutions at Various Concentrations and Temperatures". Chem. Ing. Tech., 22 : 54;1950.
115. Riedel, L., "The Determination of the Thermal Conductivity and the Specific Heat of Various Mineral Oils". Chem.-Ing.-Tech., 22 : 107;1950.

116. Riedel, L., "Thermal Conductivity of Aqueous Solutions of Strong Electrolytes". Chem.-Ing.-Tech., 23 : 59;1951.
117. Riedel, L., "New Thermal Conductivity Measurements for Organic Liquids". Chem.-Ing.-Tech., 23 : 321;1951.
118. Riedel, L., "Thermal Conductivity Measurements on Mixtures on Various Organic Compounds with Water". Chem.-Ing.-Tech., 23 : 465;1951.
119. Riedel, L., Chem.-Ing.-Tech., 27 : 209;1955.
120. Romaine, O., "How to Calibrate Thermocouples to High Accuracies". Space Aeronautics, 35 : No. 5 : 89;1961.
121. Rumford, B., Phil. Trans., 76 : 273;1786.
"Essays", 2 :199;1800.
Nicholsons J., 14 : 353;1806.
"Works" Boston, 1 : 239;1870.
122. Sakiadis, B.C. ; and Coates, J., "A Literature Survey of the Thermal Conductivity of Liquids". Bull. Engng. Expt. Sta., Louisiana State Univ., La., No. 34, 1952.
123. Sakiadis, B.C. ; and Coates, J., Bull. Engng. Expt. Sta., Louisiana State Univ., ; No. 35, 1953 : no. 45, 1954 : No. 48, 1954.
124. Sakiadis, B.C. ; and Coates, J., "Studies of Thermal Conductivity of Liquids". J.A.I.Ch.E., 1 : No. 3 : 275;1955.
125. Saunders, A.M.; Fishenden, M.; and Mansion, H.D., Engineering, 139 : 483;1935.
126. Scheffy, W.J. ; and Johnson, E.F., "Thermal Conductivities of Liquids at High Temperatures". J. Chem. Eng., Data 6 ; No. 2 : 245;1961.
127. Schleiermacher, A.L.E.F., Wiedemann Annalen Physik, 34; 1888.
128. Schmidt, R.J. ; and Milverton, S.W., Proc. Roy. Soc., A 152 : 586;1935.
129. Schmidt, R.J. ; and Saunders, O.A., Proc. Roy. Soc., A 165 : 216;1938.
130. Schmidt, E. ; and Sellschopp, W. ; Forschungsh. Ver. Dtsch. Ing., 3 : 277, 285;1932.

131. Schmidt, E. ; and Leidenfrost, W., *Forschungsh*, 21 : 176;1955.
Chem.-Ing.-Tech., 26 : 35;1954.
132. Schwab, F.W. ; and Smith, E.R., "Calculation of Temperature in Platinum Resistance Thermometry". *J. of Research, N.B.S.*, Washington, 34 : 360;1945.
133. Seshadri, T.N. ; and Jain, S.P., "A Constant Ice-Point Junction for Thermocouples in Continuous Use for Long Periods", *J. Sci. Industr. Research.*, 20 : No. 4 : 161;1961.
134. Shiba, H., *Bull. Inst. Phys. Chem. Res. Tokyo.* 16 : 205;1931.
135. Smith, J.F.D., "Thermal Conductivity of Liquids". *Ind. Eng. Chem.*, 22 : 1246;1930.
136. Smith, J.F.D., "Dimensional Analysis Applied to the Thermal Conductivity of Liquids". *Ind. Eng. Chem.*, 23 : 416;1931.
137. Smith, J.F.D., "Thermal Conductivity of Gasoline". *J.A.S.M.E.*, 56 : 307;1934.
138. Smith, J.F.D., "The Thermal Conductivity of Liquids". *Trans. A.S.M.E.* 58 : 719;1936.
139. Spencer, A.N. ; and Todd, M.C.J., "Viscosity and Thermal Conductivity of Liquid Boron Trifluoride". *British J. App. Phys.*, 11 : 60;1960.
140. Soonalawa, M.F., "Thermal Conductivity of Water". *Indian J. Phys.*, 18 : 71;1944.
141. Thermistor Manual. Fenwal Electronics Inc., Framingham, Mass., No. EMC-4.
142. Thermistor Probes. Fenwal Electronics Inc., Framingham, Mass., No. EM 13A.
143. Thermistors - Considerations in Testing. Fenwal Electronics Inc., Framingham, Mass.
144. Thomson, T., *Nicholson's J.*, 4 : 529;1801.
145. Timrot, D.L.; and Vargaftik W.B., "Heat Conduction of Water at High Temperatures". *J. Tech. Phys. (USSR)*, 10 : 1063;1940.
146. Tyrrell, H.J.V., "Diffusion and Heat Flow in Liquids". Butterworths Press. 1961.

147. Uhlir, A., "Thermal Conductivity of Fluid Argon and Nitrogen".
J. Phys. Chem., 20 : 462;1952.
148. U.S. Dept. of Comm., "Attaching Thermocouples by Capacitance
Welding". Bull. P.B. 121901.
149. Van Der Held, E.F.M. ; and Van Drunen, F.G., "A Method of Measuring
the Thermal Conductivity of Liquids". Physica, 15 : 865;1949.
150. Van Der Held, E.F.M. ; Hardebol, J. ; and Kalshoven, J., "On the
Measurement of the Thermal Conductivity of Liquids by a Non-
Stationary Method". Physica, 19 : 217;1953.
151. Vargaftik, N.B. ; and Kezzheutsev, W., Shur. Fig. Khim., 24 : 718;
1950.
152. Vilim, O., "Thermal Conductivity of Hydrocarbons". Coll. Trav.
Chim. Tcheosl, 25 : 993;1960.
153. Vines, R.G., "Measurement of Thermal Conductivity of Gases at High
Temperatures". Trans. A.S.M.E. ; j. of Heat Transfer;
Series C ; 82 : 48;1960.
154. Von Aubel, E.Z., Phys. Chem., 28 : 336;1899.
155. Wakayama, K. ; and Hattori, T., "Apparatus for Thermal Conductivity
Measurement, with Automatic Control of Temperature Difference".
J. Appl. Phys., Japan. ; 28 (4) : 249;1959.
156. Waterman, T.E., "Thermal Conductivity of Liquid Ozone". Symposium
on Thermal Properties. Heat Transfer Div., A.S.M.E., 301;1959.
157. Weber, H.F., Ann. Phys., 10 : 103, 304, 472;1880.
11 : 345;1880.
158. Winkelmann, Ann. Phys., 153 : 481;1874. 10 - 668;1880.
159. Winkelmann, Ann. Phys., 29 : 68;1886.
160. Yang, L.M., Nature, London. 161 : 523;1948.
161. Zaloudek, F.R., "Experimental Determination of the Thermal Conductivity
of Liquids". M.S. Thesis, Purdue Univ. Lafayette, Ind.
1956..
162. Ziebland, H. ; and Burton, J.T.A., "The Thermal Conductivity of
Heavy Water Between 75° and 260°C at Pressures up to 300
Atmospheres". International J. Heat and Mass Transfer, 1 :
242;1960.

163. Ziebland, H., "The Thermal Conductivity of Toluene. New Determinations and an Appraisal of Recent Experimental Work". International J. Heat and Mass Transfer. 2 : No. 4 : 273;1961.
164. Ziebland, H. ; and Burton, J.T.A., "Transport Properties of Some Organic Heat Transfer Fluids. Thermal Conductivity of Biphenyl, Phenyl Ether, Dowtherm A. and Santowax R". Chem. Eng. Data Journal. 6 : No. 4 : 579;1961.

APPENDICES

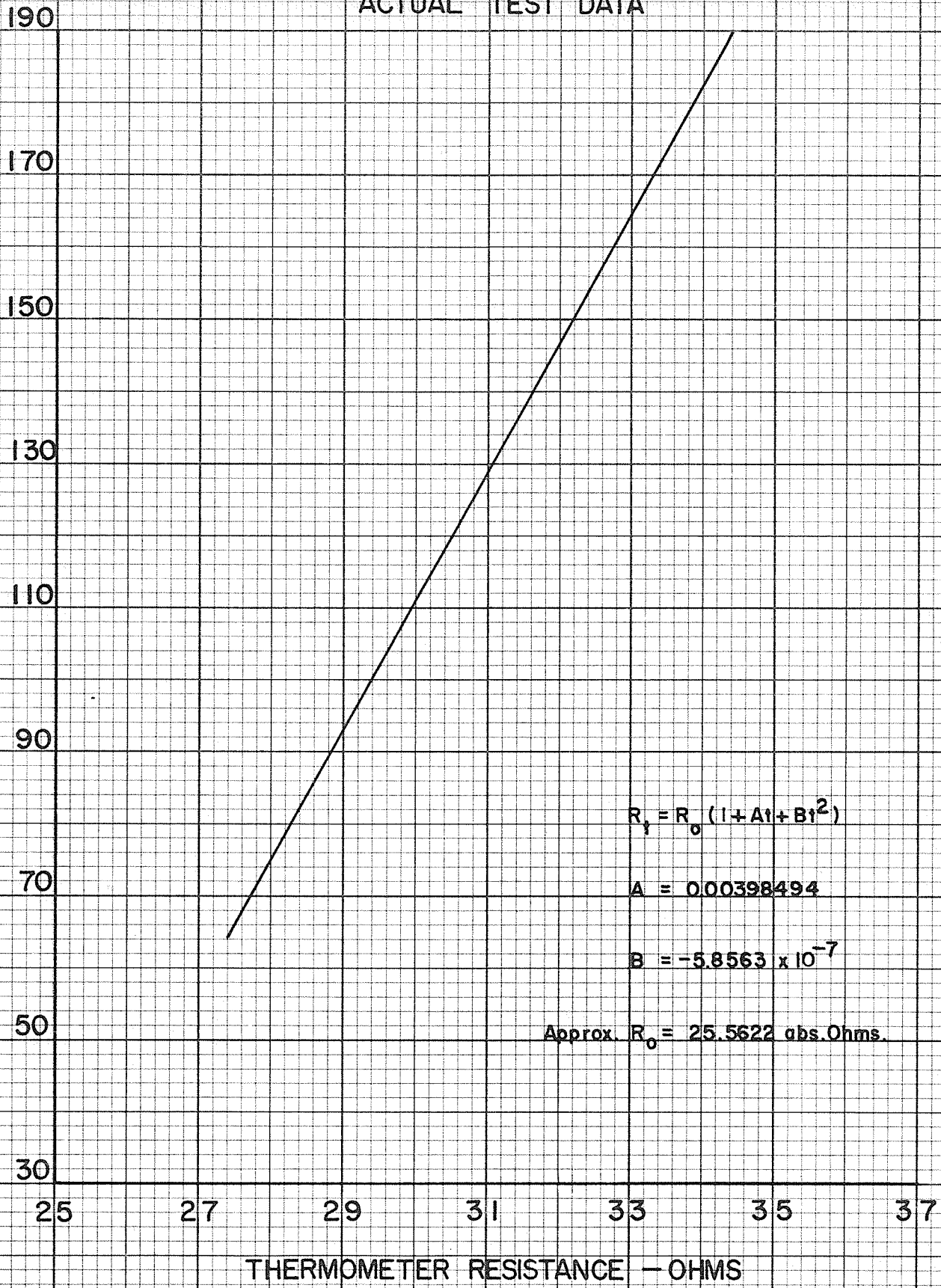
APPENDIX ITABLE 5CALIBRATION DATA FOR THE THERMAL CONDUCTIVITY APPARATUS

Bath Temperature °F	Resistance Thermometer Resistance OHMS	E.M.F. of Bath Thermocouples Millivolts	Hot-wire cell Test Section Resistance OHMS
64.65	27.4050	.9395	6.2028
69.2529	27.6640	1.076	6.2642
69.8934	27.7000	1.089	6.2719
73.5215	27.9040	1.198	6.3220
79.0394	28.2140	1.361	6.3945
86.9761	28.6594	1.595	6.5012
87.6448	28.6969	1.617	6.5142
89.5145	28.8020	1.672	6.5363
93.9875	29.0524	1.807	6.5996
99.0882	29.3380	1.960	6.6710
100.5719	29.4210	2.003	6.6918
104.8438	29.6600	2.125	6.7517
118.9162	30.4460	2.541	6.9469
123.3705	30.6944	2.688	7.0055
124.9389	30.7818	2.737	7.0261
143.206	31.8458	3.316	7.2959
149.7598	32.1623	3.491	7.3739
150.4013	32.1979	3.508	7.3797
154.1167	32.4040	3.623	7.4379
161.2603	32.8000	3.845	7.5363
167.5816	33.1500	4.036	7.6232
168.41498	33.1961	4.062	7.6311
172.4992	33.4220	4.186	7.6949
189.6291	34.3678	4.709	7.9404
195.0544	34.6668	4.882	8.0135
199.3984	34.9060	5.017	8.0497
199.515	34.9124	5.070	8.0509
200.3617	34.9590	5.048	8.0916

APPENDIX I (CONTINUED)

Bath Temperature °F	Resistance Thermometer Resistance OHMS	E.M.F. of Bath Thermocouples Millivolts	Hot-wire cell Test Section Resistance OHMS
210.1447 216.9118 221.1296	35.4970 35.8686 36.1000	5.347 5.557 5.689	8.2262 8.3218 8.3822
225.325 230.124	36.3000 36.5929	5.817 5.965	8.4419 8.5074
244.8811 250.156 251.4384 254.2546	37.4000 37.6880 37.7580 37.9116	6.379 6.542 6.598 6.654	8.7017 8.7717 8.8030 8.8262
294.4353 300.326 302.2966 306.3315	40.0955 40.4144 40.5210 40.7392	7.918 8.091 8.168 8.282	9.4020 9.4871 9.5395 9.5790
345.5708 350.3251 354.5521 355.9636	42.8532 43.1084 43.3350 43.4107	9.517 9.655 9.832 9.839	10.1571 10.2262 10.3263 10.3408
394.9518 400.066 401.7564 407.2235	45.4934 45.7655 45.8554 46.1460	11.062 11.262 11.262 11.442	10.9008 11.0052 11.0009 11.0910
443.8576 449.6398 451.0576 455.1645	48.0859 48.3910 48.3922 48.6822	12.812 12.795 12.973	11.6392 11.7352 11.7273 11.8129
493.0232 499.3929 500.2903 504.9565	50.6700 51.0031 51.0500 51.2938	14.157 14.372 14.388 14.554	12.4085 12.5010 12.5159 12.5910
544.4114 549.4856 551.2028 556.754	53.3470 53.6100 53.6990 53.9863	15.780 15.951 15.998 16.185	13.2081 13.2916 13.3227 13.4006
597.1730 599.8586 603.2084 608.3546	56.0700 56.2080 56.3800 56.6440	17.405 17.547 17.638 17.794	14.0444 14.0824 14.1408 14.2241

RESISTANCE Vs. TEMPERATURE RELATIONSHIP FOR LEEDS AND
 NORTHRUP PLATINUM RESISTANCE THERMOMETER No.1599177
 ACTUAL TEST DATA

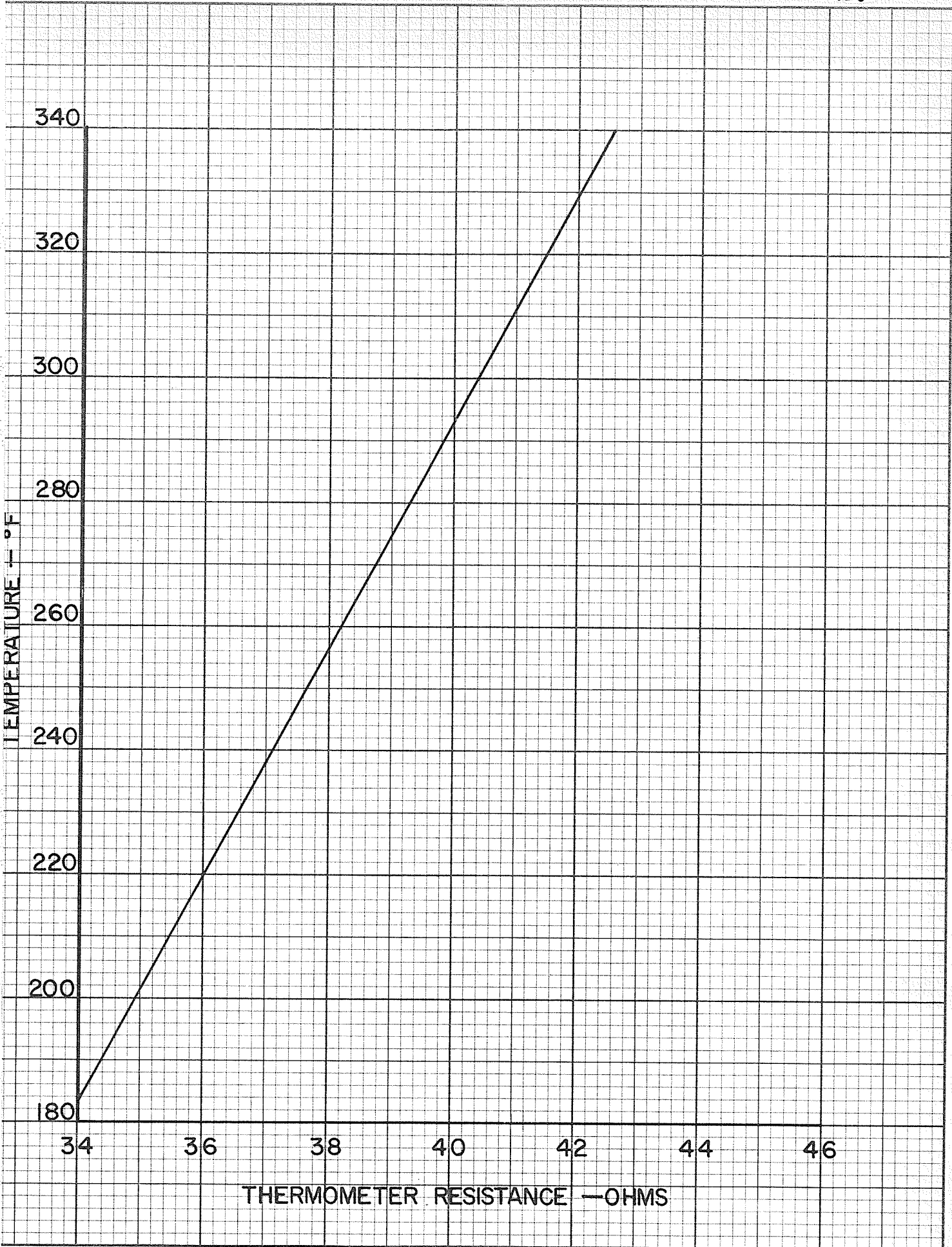


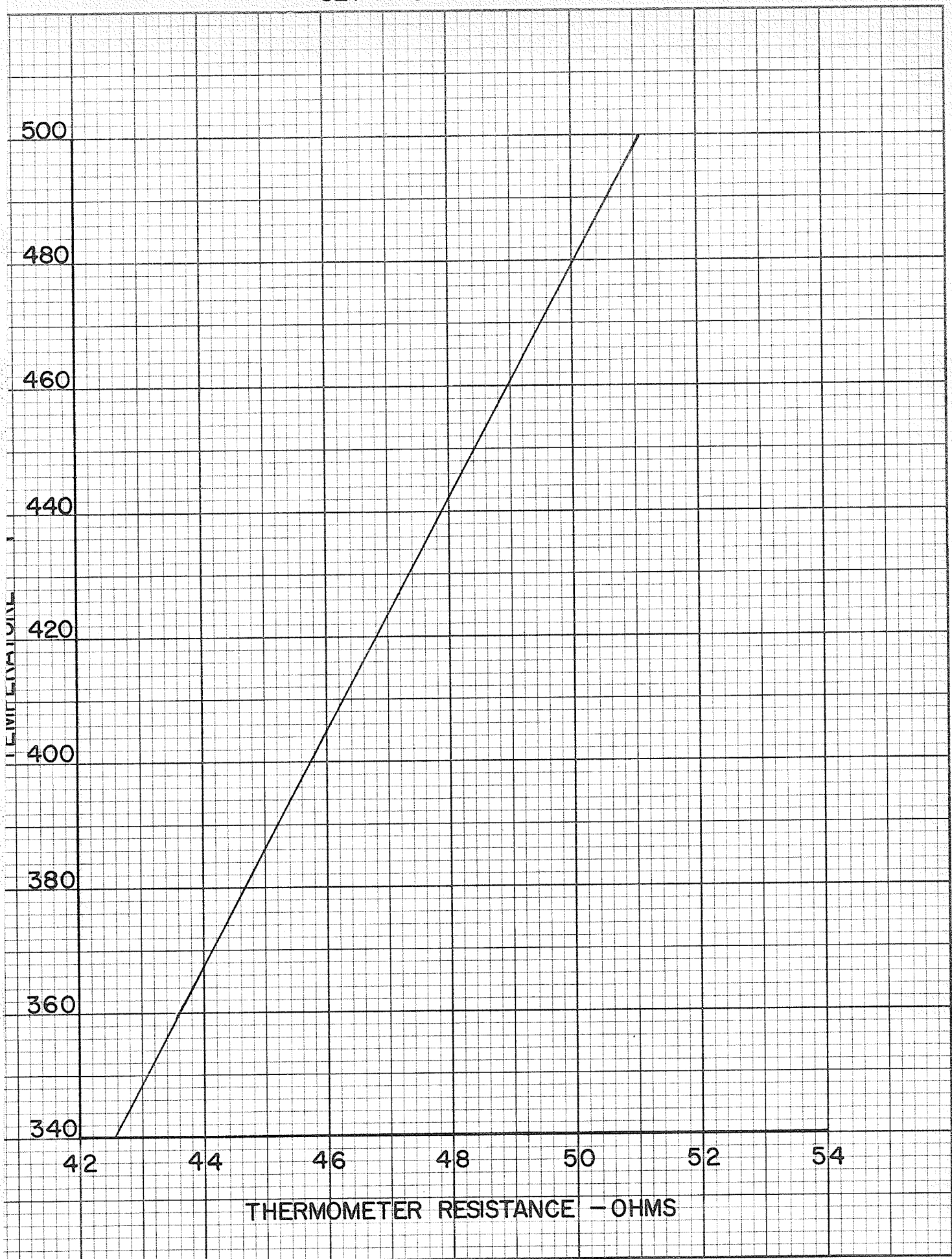
$$R_t = R_0 (1 + At + Bt^2)$$

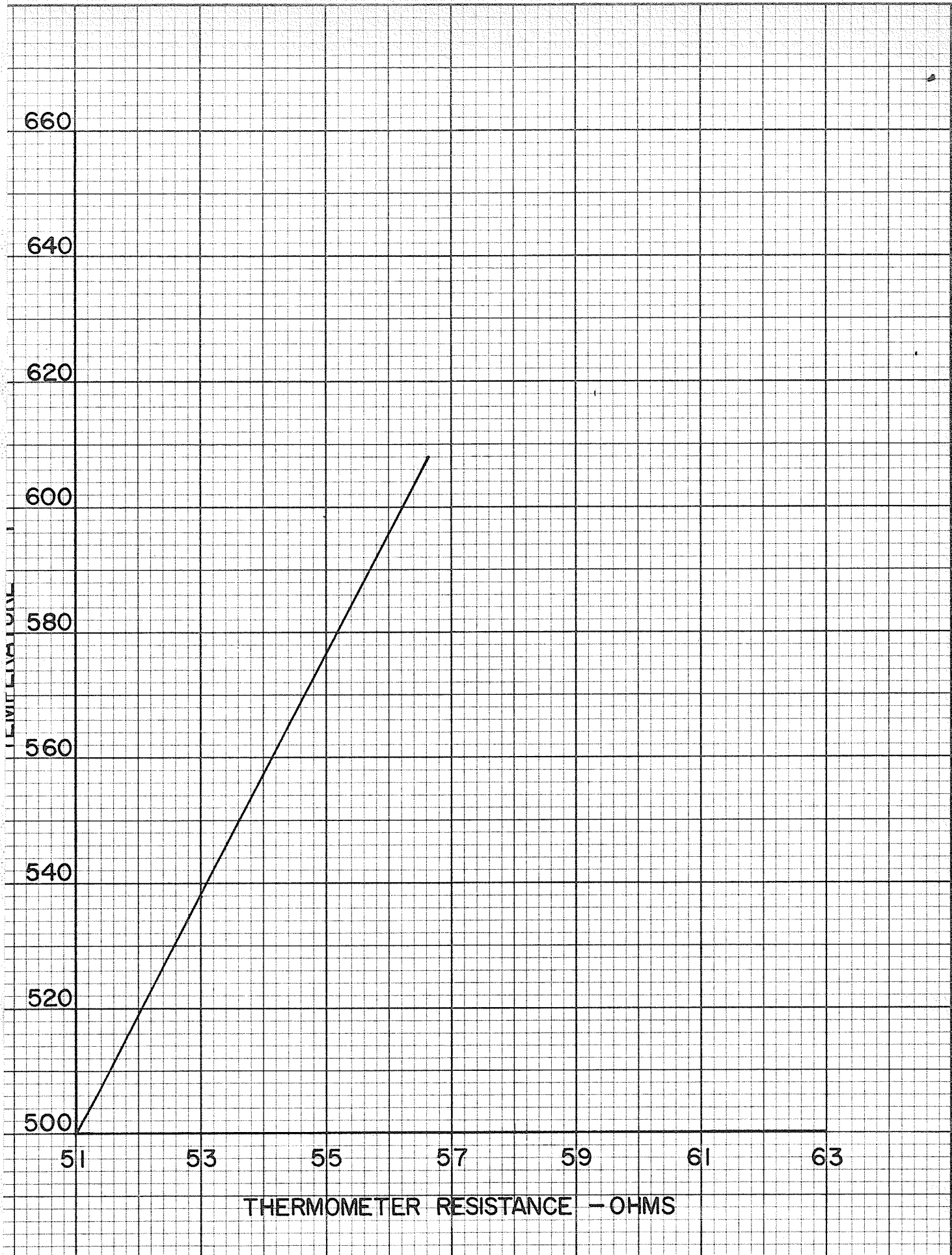
$$A = 0.00398494$$

$$B = -5.8563 \times 10^{-7}$$

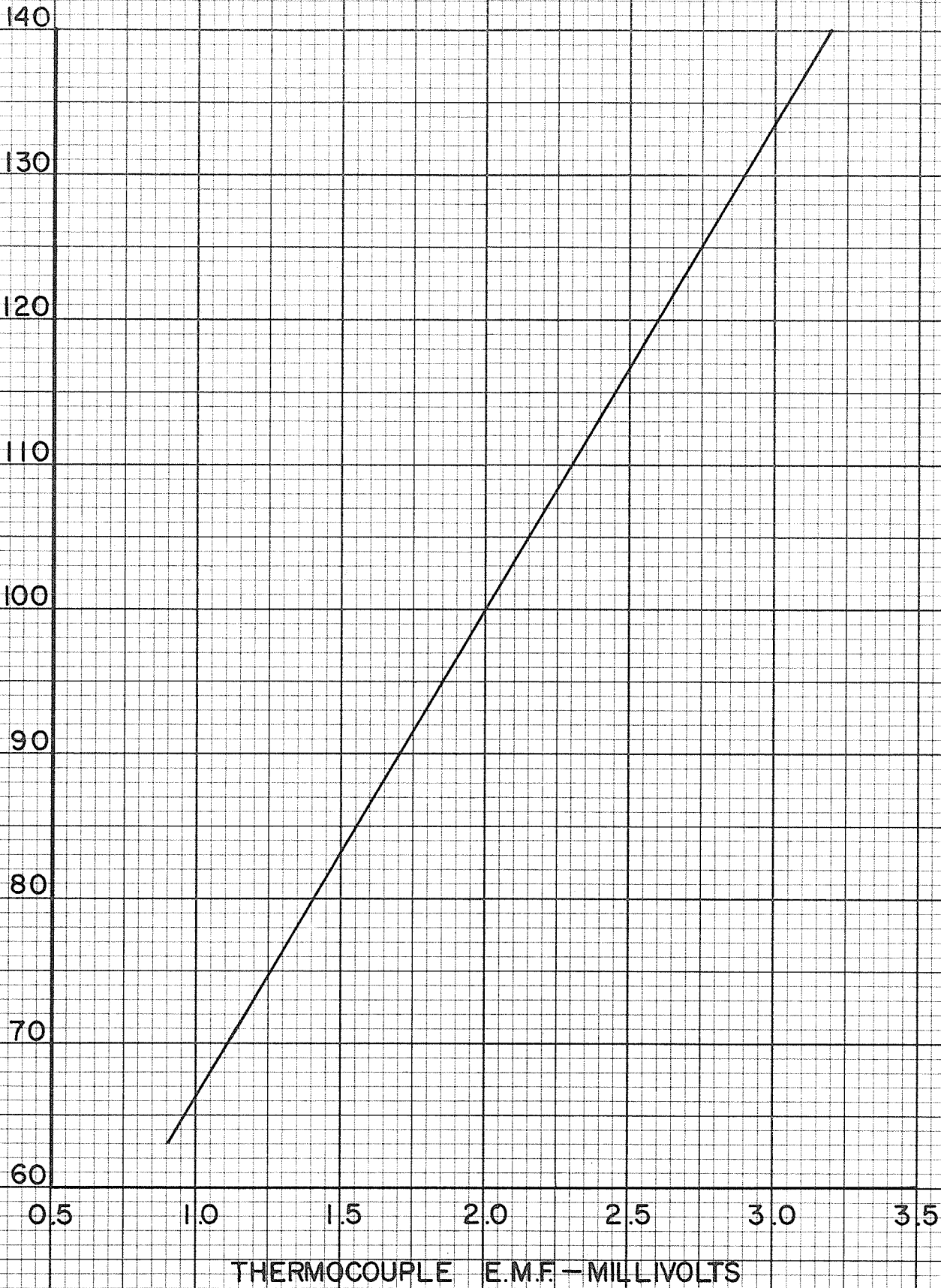
Approx. $R_0 = 25.5622$ abs. Ohms.

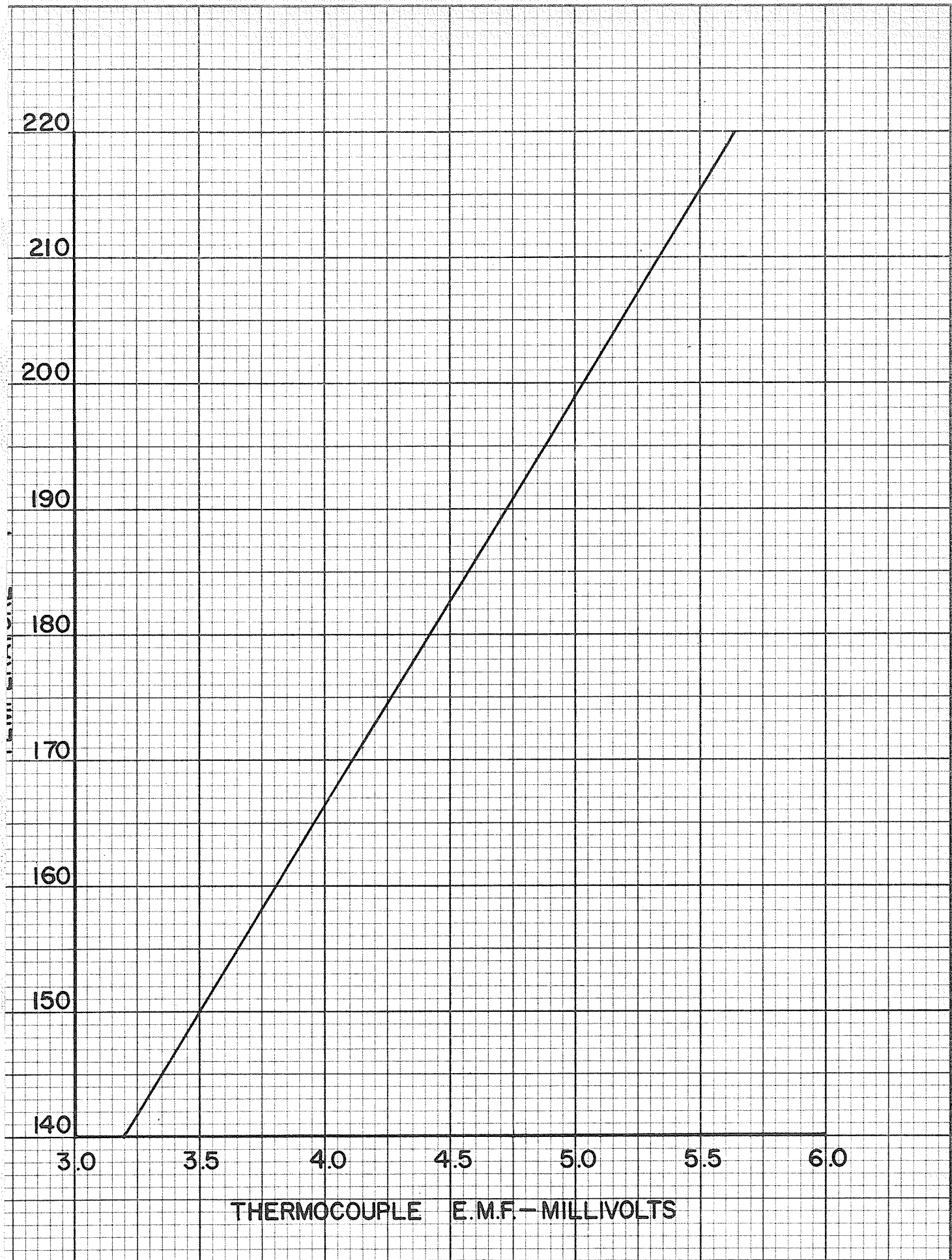


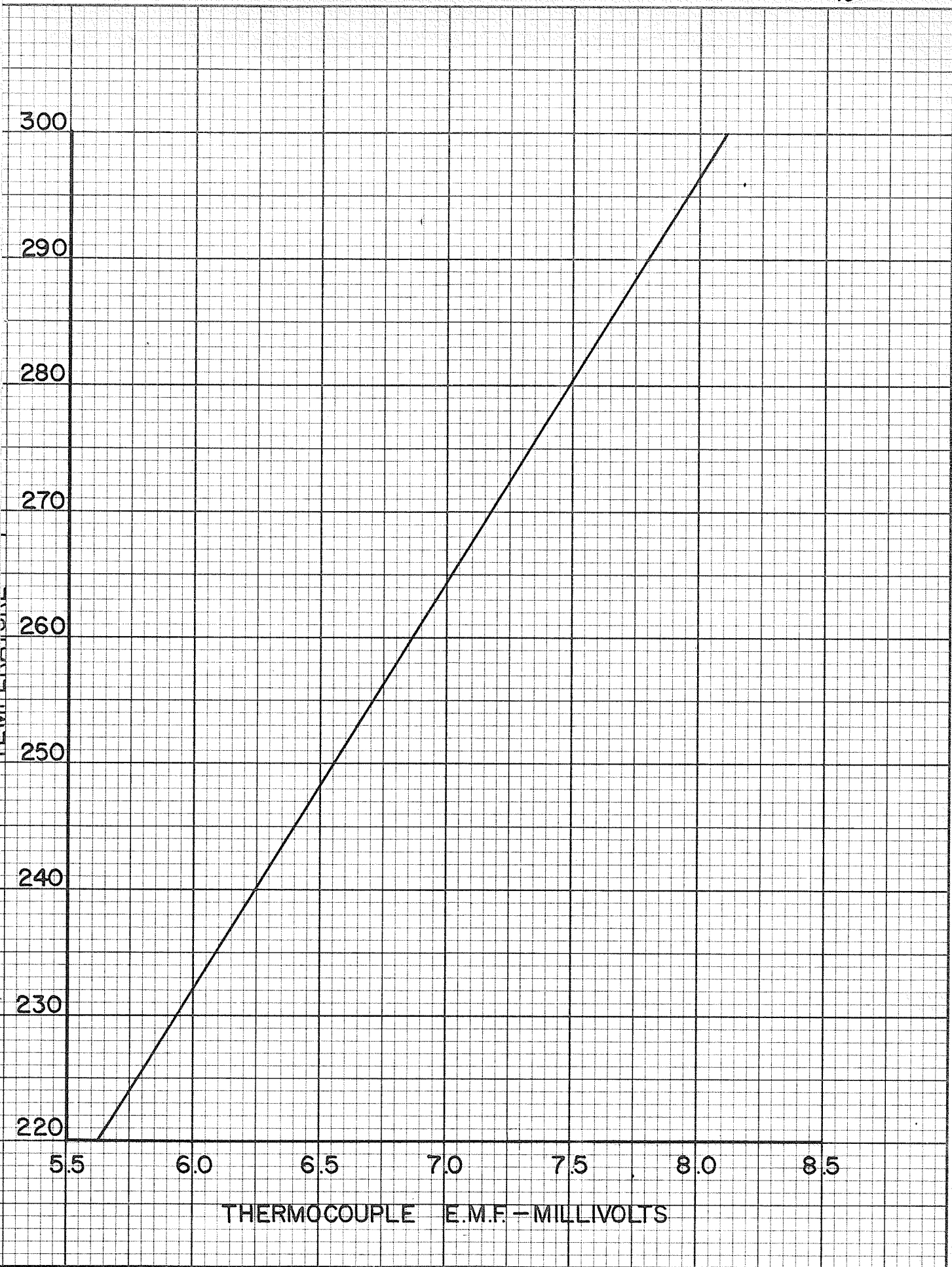


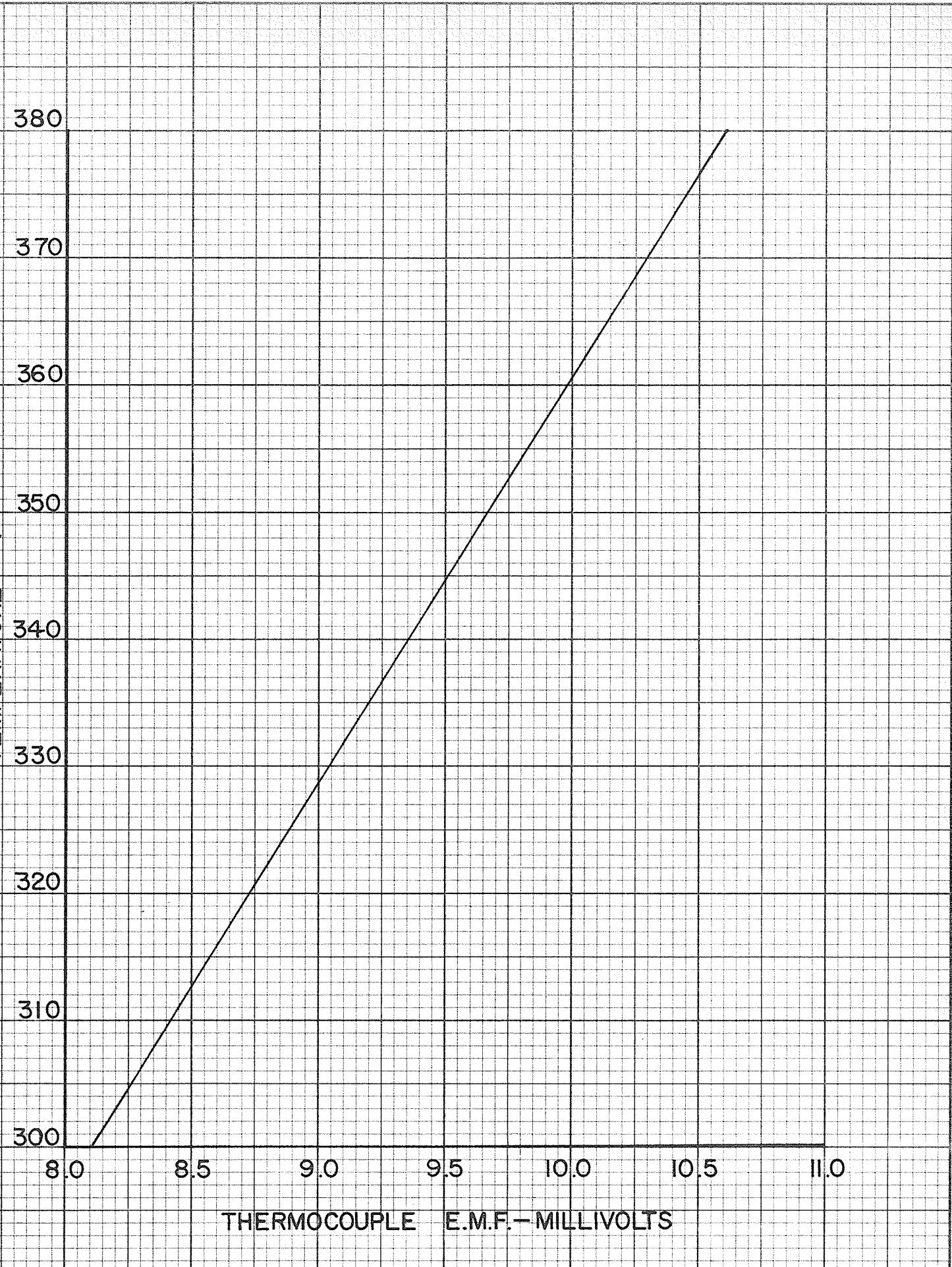


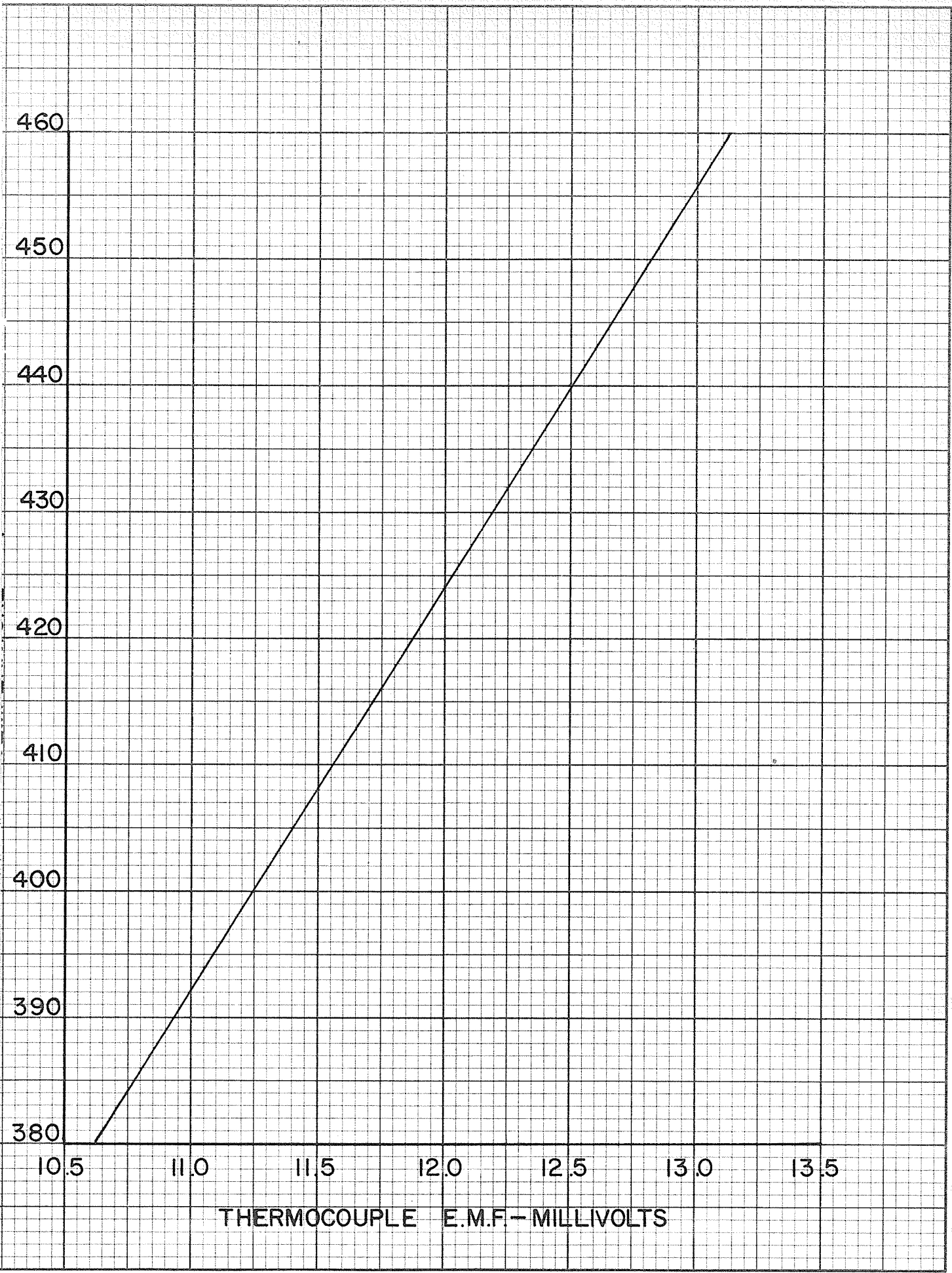
CALIBRATION OF THE CONSTANT TEMPERATURE
OIL BATH THERMOCOUPLES

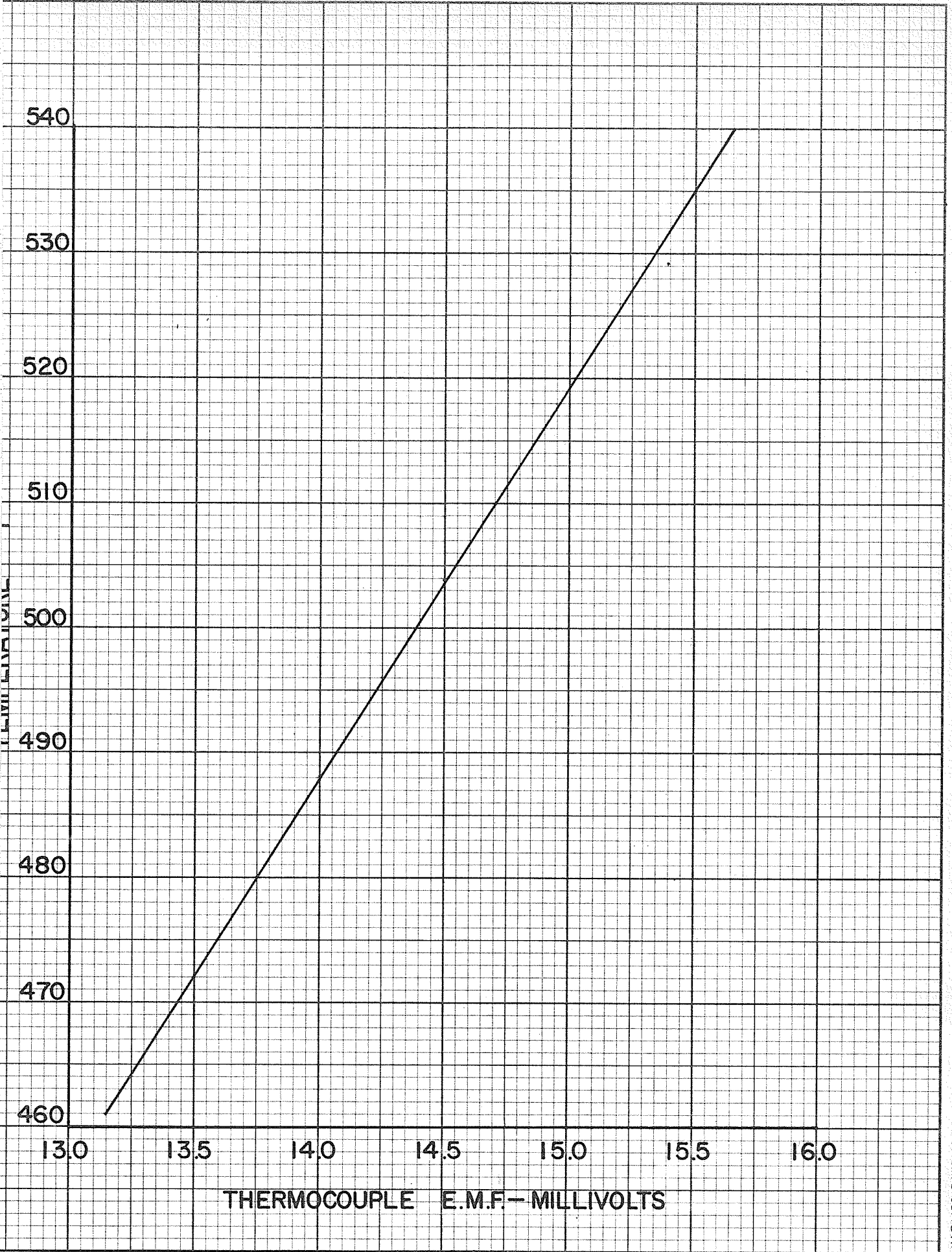












620

610

600

590

580

570

560

550

540

15.5

16.0

16.5

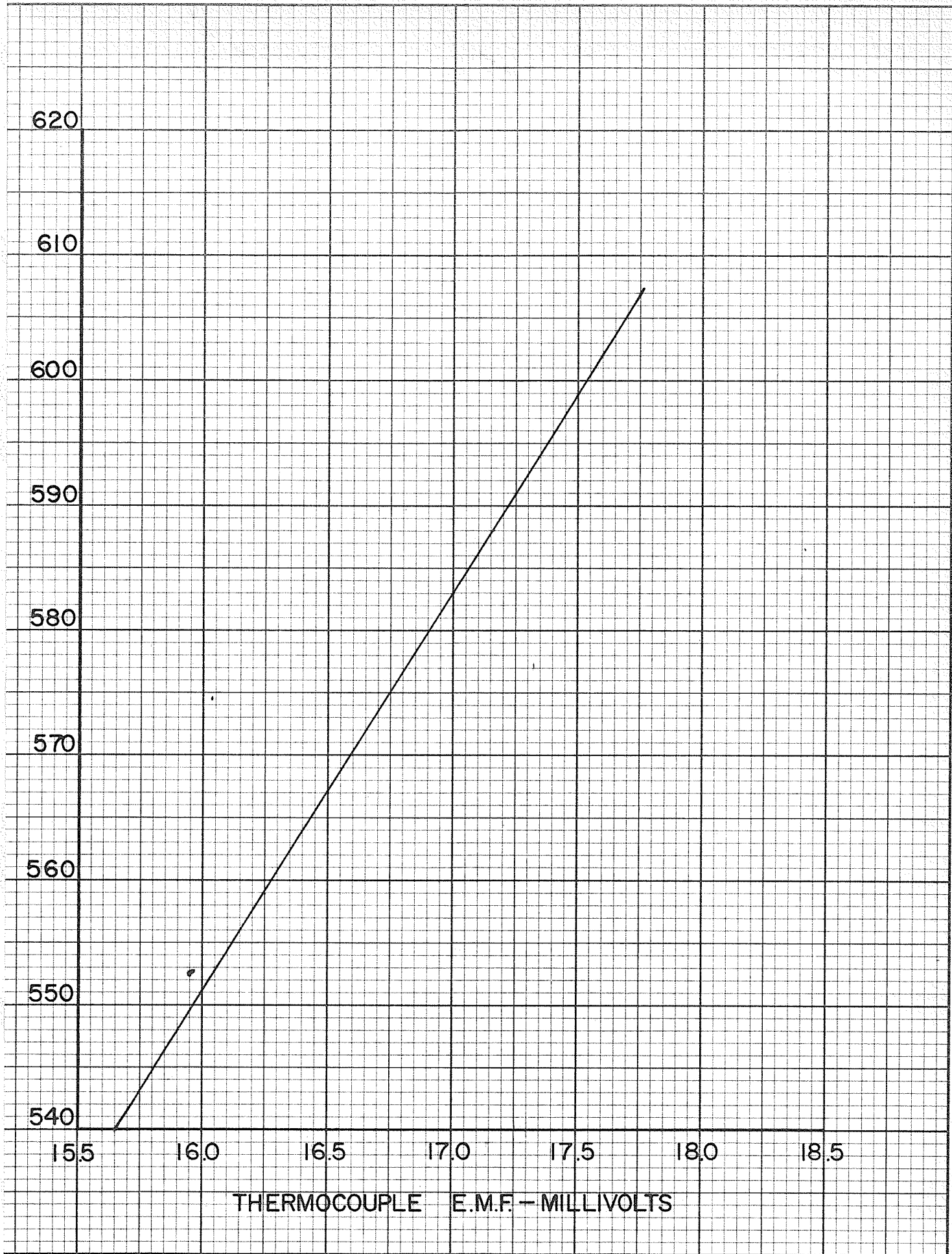
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17.5

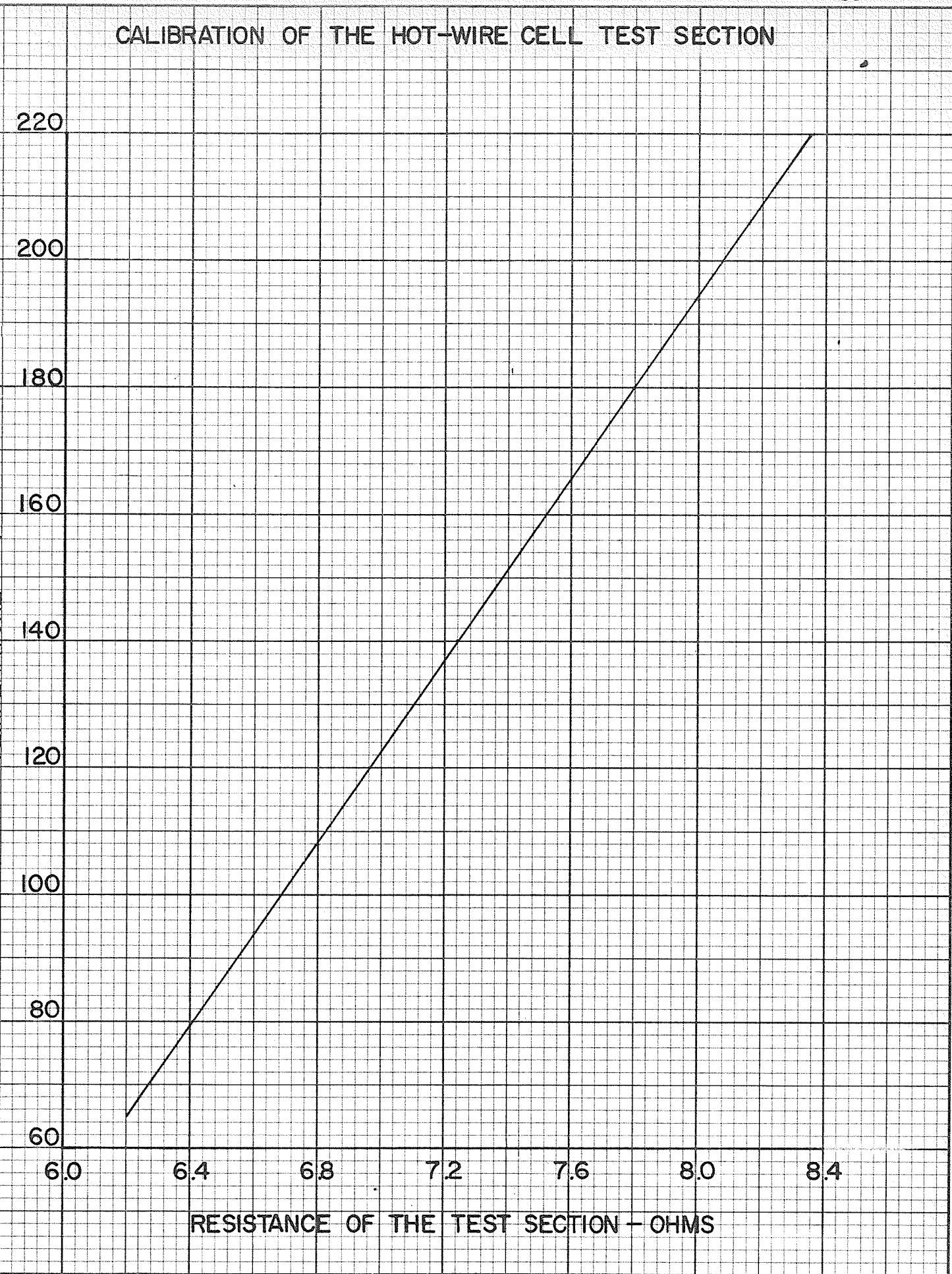
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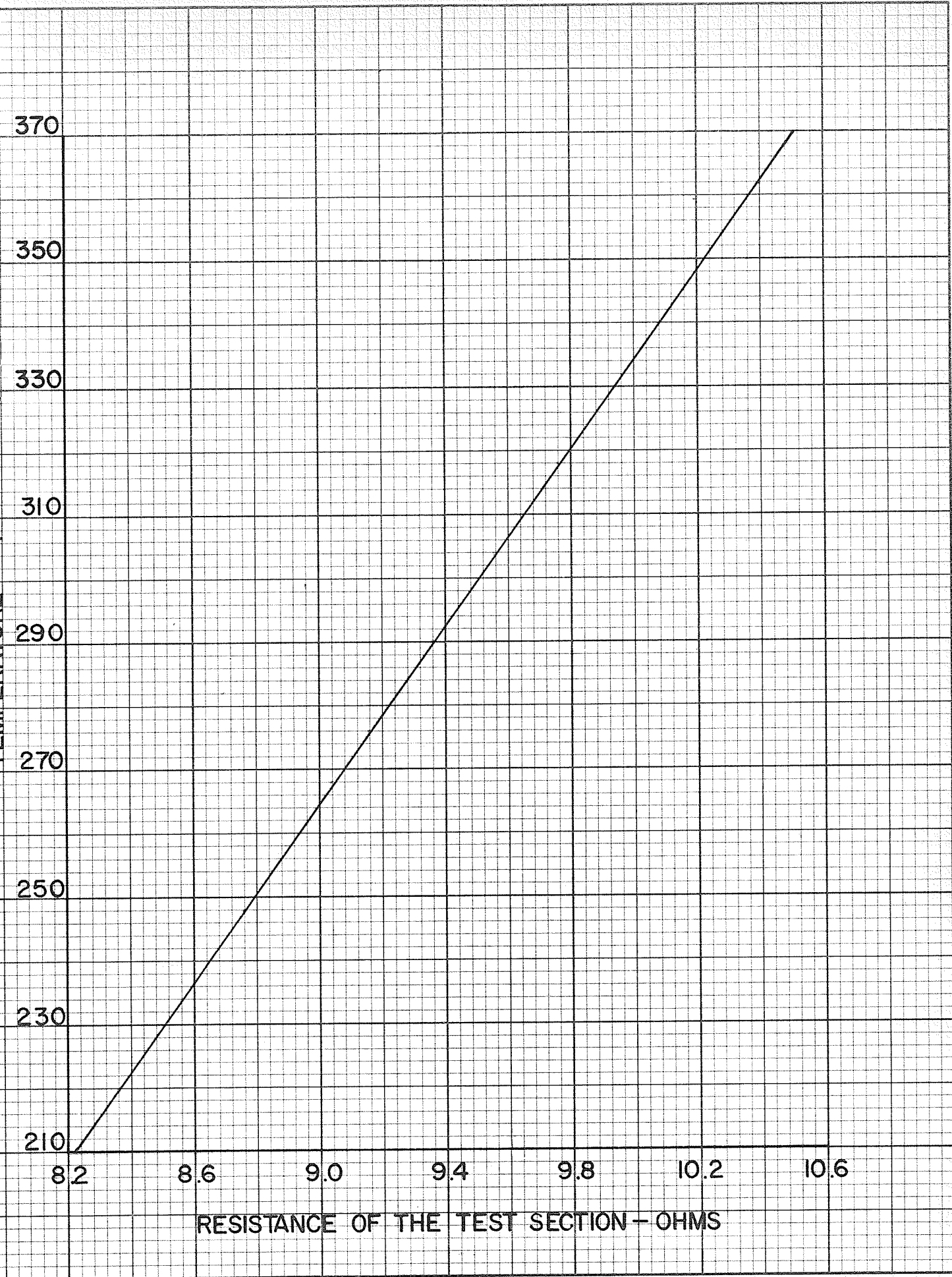
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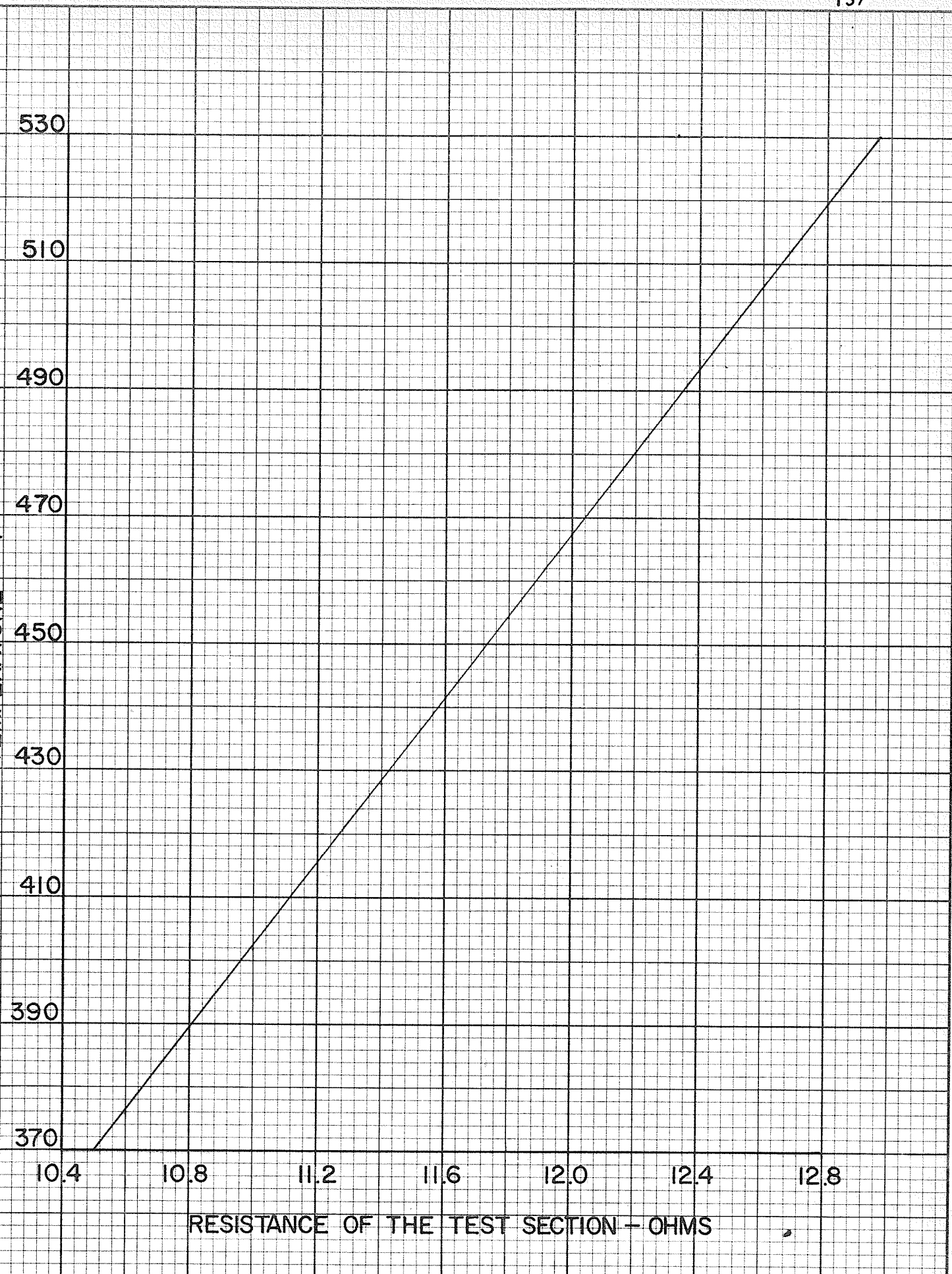
THERMOCOUPLE E.M.F. - MILLIVOLTS

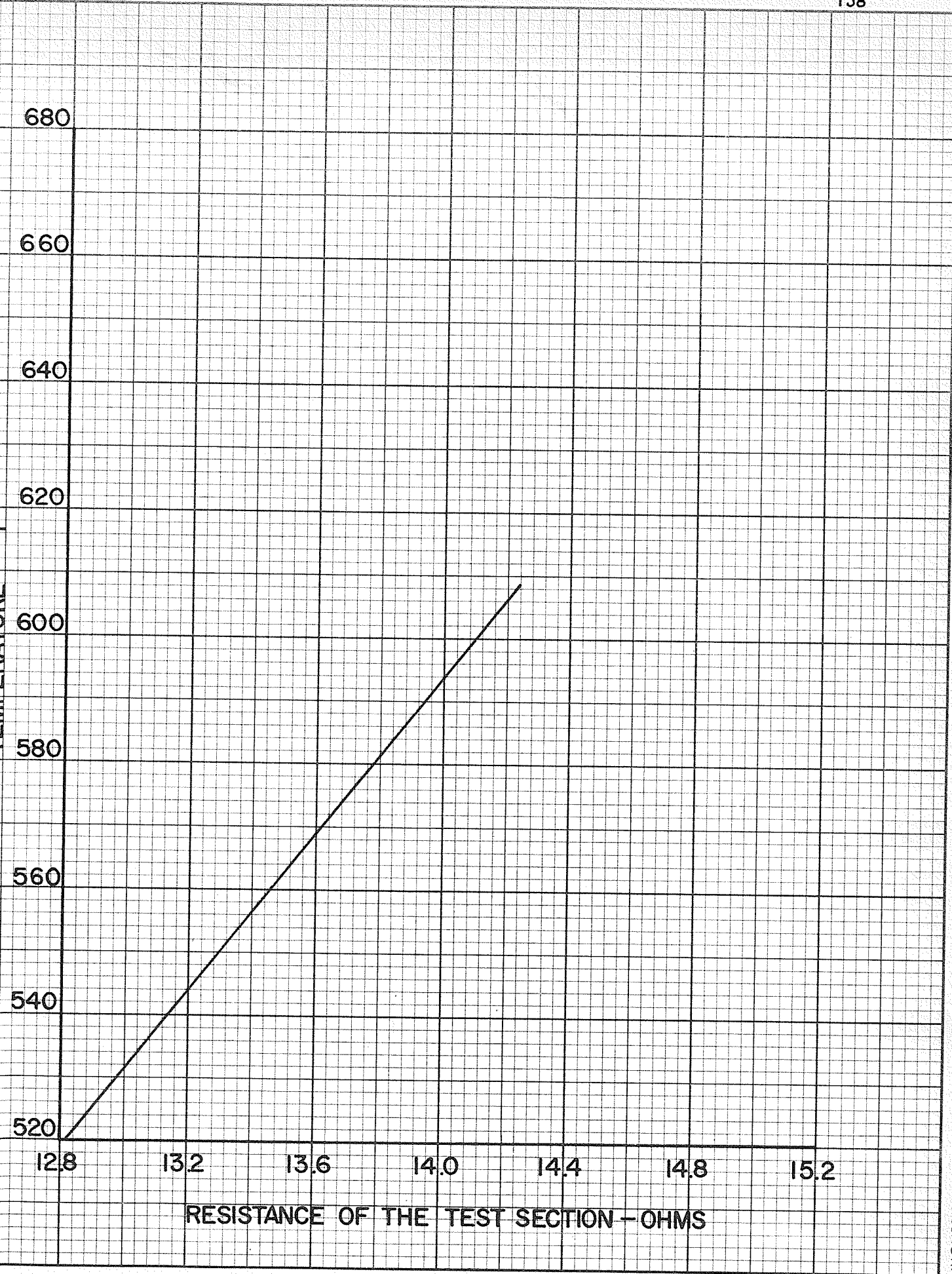


CALIBRATION OF THE HOT-WIRE CELL TEST SECTION









APPENDIX IITABLE 6(1) EXPERIMENTAL DATA AND PHYSICAL PROPERTIES OF CARBON TETRACHLORIDE

Test Temperature °F	Thermal Conductivity of Pyrex Brand Glass No. 7740 Btu/(Hr)(Ft)(°F)	Average Temperature drop across the liquid film °F	Heat Dissipated in the test section. Btu/Hrx10 ⁴	Thermal Conductivity of the liquid Btu (Hr)(Ft)(°F)	(N _{GR})(N _{PR})
69.25	0.551*	0.746	293.30	0.0692	4465
87.64	0.564	0.653	304.44	0.0821	4780
100.57	0.573	0.618	312.37	0.0892	5200
124.94	0.589	0.698	327.13	0.0825	7000
150.40	0.607	0.686	342.82	0.0880	9340
168.41	0.620	0.728	353.938	0.0856	11200

Density at 77°F	: 98.952 lbs/ft ³
Boiling range	: 169.88 - 170.24°F
Residue after evaporation	: 0.001%
Sulphur Compounds	: 0.002%
Manufacturer	: Fisher Scientific Co. Limited 245 Carlaw Ave., Toronto 8.
Catalogue Number	: C-199

*Interpolated values from data supplied by
Corning Glass Works, Corning, New York.

TABLE 7

(2) EXPERIMENTAL DATA AND PHYSICAL PROPERTIES OF TOLUENE

Test Temperature °F	Thermal Conductivity of Pyrex Brand Glass No. 7740 Btu/(Hr)(Ft)(°F)	Average Temperature drop across the liquid film °F	Heat Dissipated in the test section Btu/Hrx10 ⁴	Thermal Conductivity of the liquid Btu/(Hr)(Ft)(°F)	(N _{GR})(N _{PR})
69.89	0.551	0.715	293.79	0.0723	4850
86.98	0.563	0.690	304.51	0.0777	5360
99.09	0.572	0.713	311.63	0.0769	5980
123.37	0.588	0.741	325.67	0.0773	7220
149.76	0.607	0.758	342.23	0.0795	9000
167.58	0.619	0.750	353.40	0.0792	10400
195.05	0.638	0.790	369.68	0.0823	12700
216.91	0.653	0.746	381.36	0.0901	14950
230.12	0.662	0.767	389.87	0.0895	16800

Specific gravity : 0.866
 Boiling range : 230.72 - 231.44°F
 Residue after evaporation : 0.000%
 Sulphur compounds : 0.000%
 Manufacturer : Fisher Scientific Co. Ltd.,
 245 Carlaw Avenue, Toronto 8.
 Catalogue number : T-324

TABLE 8

(3) EXPERIMENTAL DATA AND PHYSICAL PROPERTIES OF HB-40

Test Temperature °F	Thermal Conductivity of Pyrex Brand Glass No. 7740 Btu/(Hr)(Ft)(°F)	Average Temperature drop across the liquid film °F	Heat Dissipated in the test section Btu/Hrx10 ⁴	Thermal Conductivity of the liquid Btu/(Hr)(Ft)(°F)	(N _{GR})(N _{PR})
250.16	0.676	1.278	397.71	0.0545	494
300.33	0.711	1.226	427.72	0.0611	875
350.33	0.745	1.181	458.18	0.0680	1312
401.76	0.777	1.186	489.32	0.0723	1810
451.06	0.790	1.137	521.26	0.0805	2335
500.29	0.803	1.097	552.57	0.0885	4030
551.20	0.817	1.049	583.90	0.0978	5620
603.21	0.831	0.924	617.23	0.1177	6420

HB-40 : Santowax OMP Hydrogenated to
40%

Boiling range : 644 - 744.8°F.

TABLE 9

(4) EXPERIMENTAL DATA AND PHYSICAL PROPERTIES OF HYDROGENATEDSANTOWAX OM

Test Temperature °F	Thermal Conductivity of Pyrex Brand Glass No. 7740 Btu/(Hr)(Ft)(°F)	Average Temperature drop across the liquid film °F	Heat Dissipated in the test section Btu/Hrx10 ⁴	Thermal Conductivity of the liquid Btu/(Hr)(Ft)(°F)	(N) (N) GR PR
251.44	0.677	1.205	399.34	0.0580	1930
302.30	0.712	1.252	431.04	0.0603	4500
354.55	0.748	1.274	464.24	0.0638	7320
400.07	0.776	1.307	493.25	0.0661	10040
449.64	0.789	1.342	523.03	0.0683	13580
499.39	0.803	1.363	554.33	0.0713	17260
549.49	0.816	1.367	586.03	0.0751	22300
599.86	0.830	1.309	614.62	0.0823	26700

Santowax OM

: Hydrogenated to 13%

Composition of Santowax Om before Hydrogenation.

Biphenyl : 3.2%

Ortho Terphenyl: 61.5%

Meta Terphenyl : 7.8%

Para Terphenyl : 7.8%

Liquidus point : 105.8°F

Boiling Point : 626°F

APPENDIX IIIDESIGN DETAILS OF AUXILIARY EQUIPMENT1. THE CONCENTRIC CYLINDER CELL

An apparatus of the concentric cylinder type has been used by a variety of workers for the steady state measurements of the thermal conductivity of liquids. The cylindrical shape was chosen for convenient control of heat loss, and the rugged construction of the cell makes it suitable for measurements at high temperatures and pressures.

It is recommended^{44,146} that when the liquid is contained either between horizontal or vertical concentric cylinders, convection can be avoided by using a thin liquid layer and a small temperature difference across the layer, so that the product of Grashof and Prandtl numbers is less than 1000¹⁴⁶. If the liquid is contained between vertical concentric cylinders and if the above mentioned conditions prevail, heat will be transferred by pure conduction over the major portion of the layer. At the lower and upper ends of the layer, over a height equal to the layer thickness, a non-linear temperature drop across the layer will exist⁴⁴ if no thermal guarding is provided.

In the designed cell, the layer thickness is 0.075 inch. Using the geometry of the cell and a maximum operating temperature difference of 5°F across the layer, the product of Grashof and Prandtl numbers is less than 700 for most liquids, thus adequately meeting the recommendations for avoiding convection in the cell. The layer height has been made very much greater than the layer thickness and guard heaters are provided at the lower and upper ends of the layer. It is

envisaged, therefore, that this cell can be used for the absolute measurements of the thermal conductivity of several liquids and that the convection currents will be absent at a temperature difference of about 50°F or less across the layer.

The cell designed for this programme consists of an annular liquid layer contained between concentric brass cylinders. The designs of the cell and the constant temperature bath are such that the cell can be positioned in the bath either horizontally or vertically. This provision in design will allow the absolute thermal conductivity measurements to be made in both positions of the cell.

Figs. 9, 10 and 11, show complete details of the concentric cylinder cell. The cylinders and the end caps are made from free cutting brass, a high conductivity material. All the components of the cell are accurately machined and polished to provide an annular gap of 0.075 inch, a figure which represents a compromise between the possibility of convection at the extreme conditions for some liquids and maintenance of the effect of the geometric dimensions on the accuracy. The surface finish of the emitting and guard cylinders, and, the bore of the outer cylinder is 20 micro inches. The concentricity of the cylinders is maintained by tight and precise fitting of the end caps over the guard cylinders and into the outer cylinder. The alignment of guard cylinders with the inner cylinder is maintained by four accurately machined spacer pins made from steel. The assembly of the complete cell is shown in Fig. 11

The precise machining and finishing of all the cylinders for

DESIGN DATA

- △ EMITTING CYLINDER 1.2" O.D. x 4.5"
 - △ GUARD CYLINDER (LEFT) 1.2" O.D. x 2.25"
 - △ GUARD CYLINDER (RIGHT) 1.2" O.D. x 2.25"
- MATERIAL FOR ALL CYLINDERS: BRASS
CYLINDERS TO BE SUPPL BY U.S.M.

- ① HEATING COIL FOR △
- ② HEATING COIL FOR △
- ③ HEATING COIL FOR △

EXPERIMENTAL CONDITIONS

- ① VOLTAGE FOR OPERATION: 110 VOLT A.C. FOR INITIAL HEATING.
- ② ROOM TEMP. ± 70°F
- ③ MAXIMUM OPERATING TEMP. ± 800°F

LIMITATIONS

- 1/ HEATING COIL LENGTHS MUST BE AS SPECIFIED.
- 2/ HEATING COILS MUST BE PLACED CENTRALLY IN THE SHEATH.
- 3/ THE FINAL O.D. OF THE SHEATH MUST PROVIDE A TIGHT FIT IN A 1/2" DIAM. HOLE.

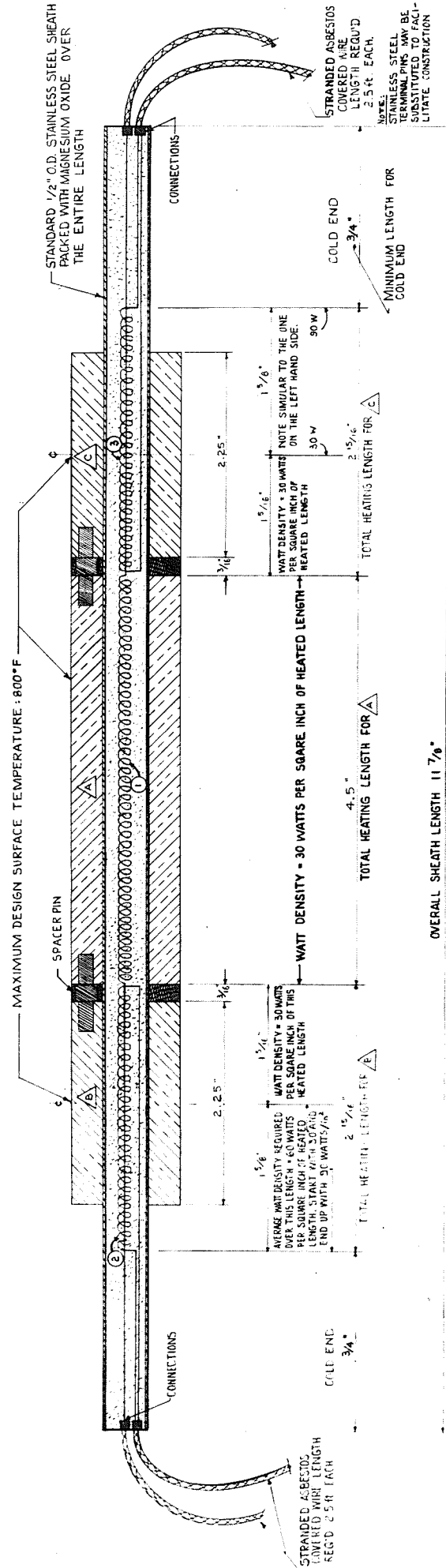
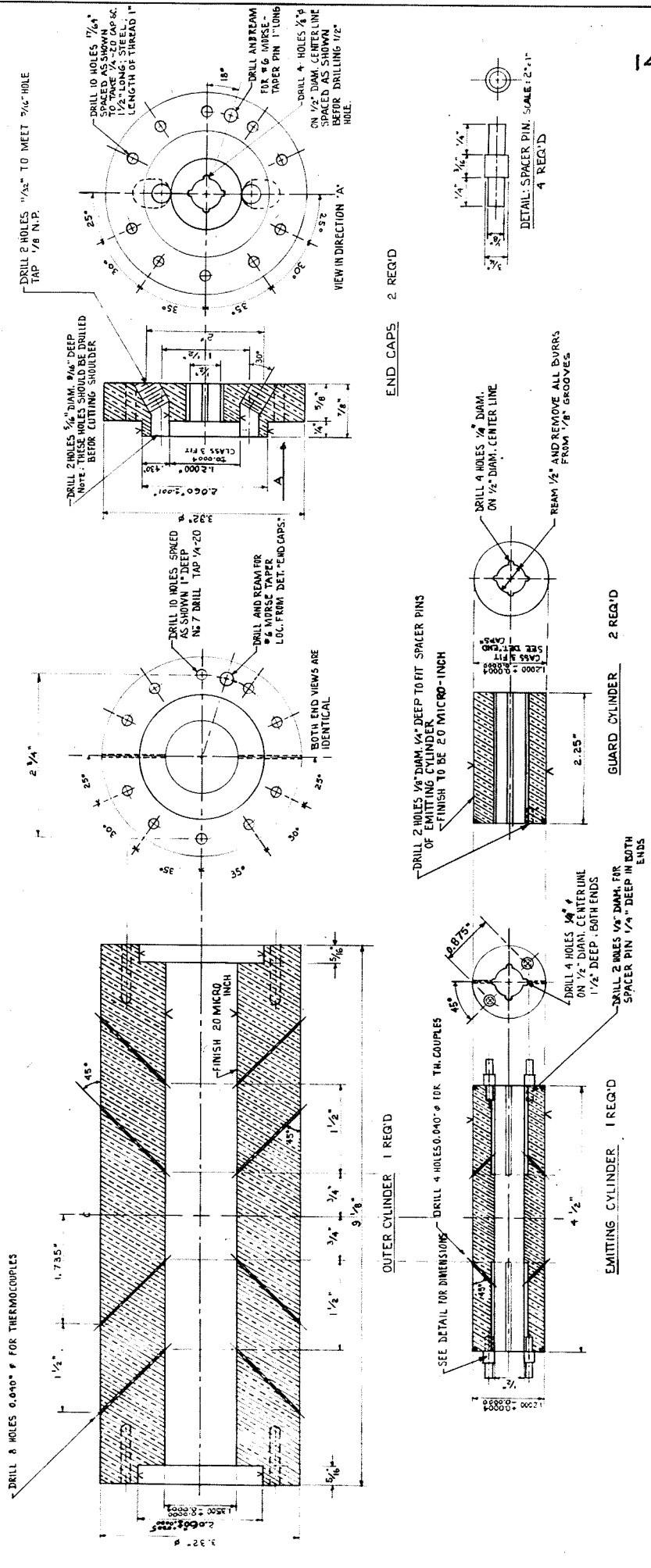


FIG. 9.

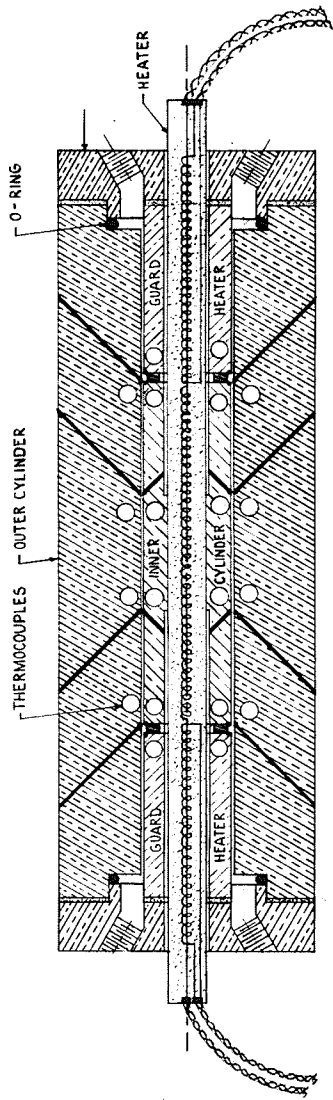
UNIVERSITY OF MANITOBA			
DEPARTMENT OF MECHANICAL ENGINEERING			
DESIGNED BY	SCALE	SHEET 3	
DATE	1/2" = 1"	No. of SHEETS 3	
APPROVED	1/2" = 1"	No. of SHEETS 3	
HEAT TRANSFER APPARATUS		DRAWING No. H 2 - 3	
(THERMAL COND. OF FLUIDS)			



NOTE: MATERIAL TO BE SUPPLIED BY U.O.P.M.
 MATERIAL FOR ALL PART SHOWN: BRASS.
 1/4" CAP SCREWS (STEEL)
 SPACER PINS AND TAPER PINS — STEEL

FIG. 10.

UNIVERSITY OF MANITOBA		DEPARTMENT OF MECHANICAL ENGINEERING	
DRAWN	SCALE	SHEET	2
DATE	7/6	NO. OF	3
DESIGNED	DEC. 28 1961	PROJECT	3
HEAT TRANSFER APPARATUS		DRAWING NO. H 2-2	
THERMAL COND. OF FLUIDS			



ASSEMBLY

FIG. 11.

UNIVERSITY OF MANITOBA			
DEPARTMENT OF MECHANICAL ENGINEERING			
DRAWN	DATE	SCALE	SHEET
DATE	DEC. 25, 1961	FULL SIZE	1
HEAT TRANSFER APPARATUS		DRAWING No.	H 2 - 1
(THERMAL COND. OF FLUIDS)			SHEETS 3

the cell was undertaken by the Bristol Aero-Industries Ltd., Winnipeg.

The heaters positioned in the emitting and guard cylinders are shown in Fig. 9. Instead of the shown flexible leads, solid terminals were used in the final construction. A Marr connector or a similar device can be used to attach a stranded asbestos wire to each terminal. The heaters consist of three parts. The middle heater supplies heat to the emitting cylinder while the remaining two are for each of the guard cylinder. An autotransformer should be used to adjust voltage to each heater.

The temperature difference across the liquid layer is to be measured by fourteen iron-constantan, "Ceramo" duplex conductor type thermocouples, and two exactly matched glass-coated thermistor beads. The characteristics of these thermistors are given in Appendix IV as these thermistors are similar to that used in the thermistor-type temperature controller.

The main feature of the thermistors is that they have a high temperature coefficient of resistance thus providing a relatively large resistance change with a small change in thermistor temperature⁵⁸. However, one major reason for the thermistors not having found a wide application for the absolute temperature measurements is that their aging characteristics have not been well established¹⁶. It is felt, however, that if a pair of exactly matched thermistors are used in the same environment then their aging characteristics will remain the same. It is recommended that the thermistors should be aged after assembly at 300°F for several days, to improve their stability¹⁴³. A direct

current of about 150 micro amperes should be passed during this aging period. When the actual tests are being performed a current of approximately 90 micro amperes should be used. An operating current of 50 to 100 micro amperes will allow good sensitivity without any appreciable self-heat of the thermistor. The thermistor resistance must be checked frequently at the ice point and it is expected that the thermistor resistance variation will not be more than ± 60 ohms in 100,000 ohms¹⁴¹.

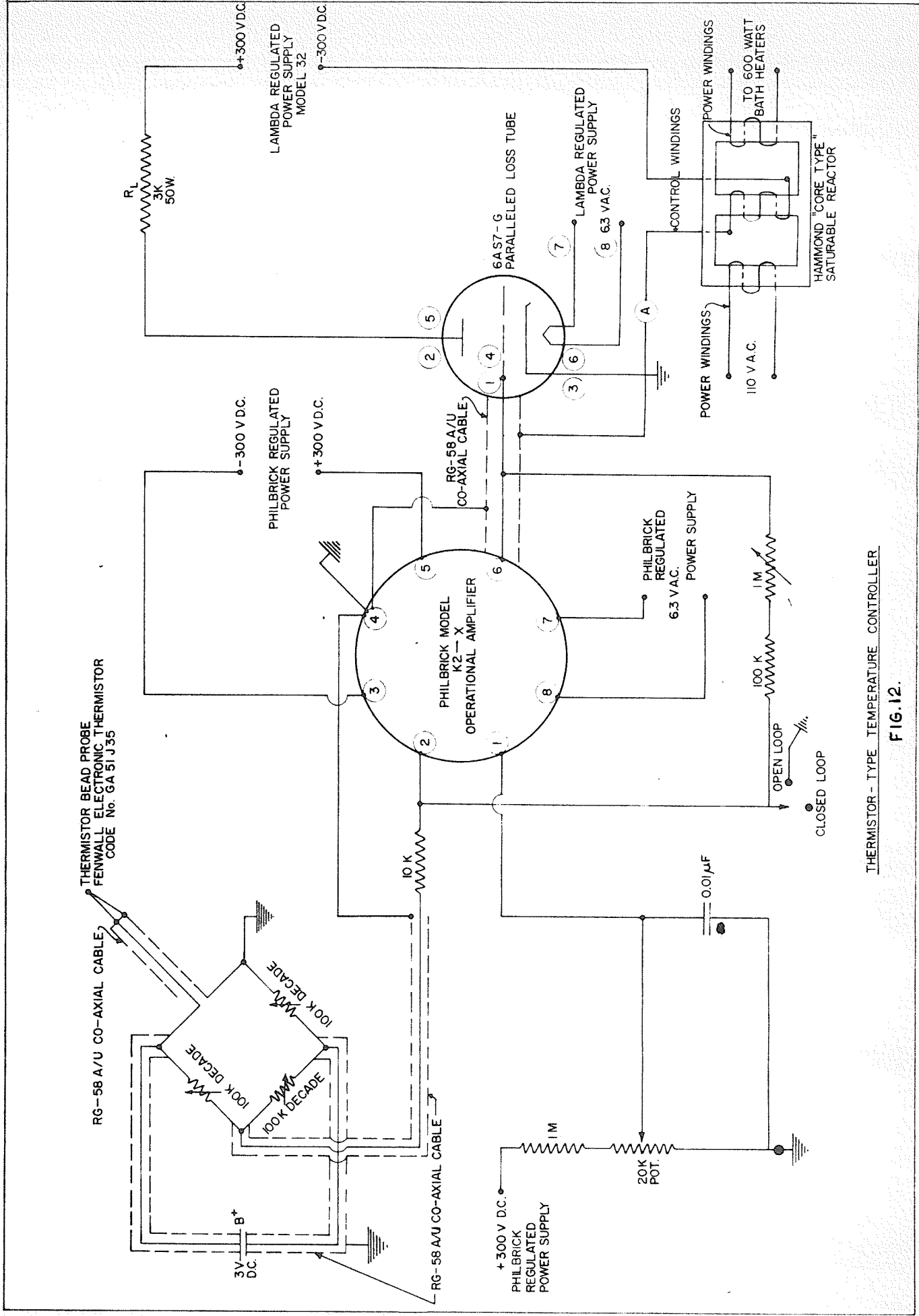
The actual experimental procedure is very similar to that described for the hot-wire cell. The annular gap between the concentric cylinder is filled with the test liquid, and the entire cell immersed in the constant temperature bath. The cell is then brought up to the test temperature by heating the bath medium to that temperature. When the steady-state has been established, the electric heater located in the emitting cylinder supplies a small amount of thermal energy which flows radially through the annular liquid layer. Guard cylinders are provided to compensate for end losses and to assure that the heat flow is radial. The quantity of heat conducted is determined by measuring the electrical input to the heater and the thermal conductivity of the liquid can be calculated from equation, IV.10.

2. THE THERMISTOR-TYPE TEMPERATURE CONTROLLER

One of the most widely employed designs of a temperature controller incorporates a circuit where an error signal from a thermocouple or a resistance thermometer causes a deflection of a galvanometer which in turn controls the bath heater through a photocell relay^{92,99}. The sensitivity of such a controller, however, is limited to $\pm 0.01^\circ\text{F}$.

For a more sensitive controller, a temperature sensing device other than a thermocouple, must be used. For example, if an iron-constantan thermocouple is used as a temperature sensing device, then for a temperature change of 0.005°F , the change in the thermocouple output or the error signal will only be 0.15 microvolts. This signal must, of course, be amplified in order to actuate a relay. The degree of amplification cannot be made too large as hum or the noise level of the amplifier and stray pick-ups will cause an erroneous signal to be fed to the galvanometer, and, consequently an incorrect control will result. The inherent problems of amplifying a small signal and the high cost of sensitive amplifiers, limit the sensitivity that can be obtained with a controller employing a thermocouple as the temperature sensing device. The use of a precision resistance thermometer as the temperature sensing unit in a control circuit is not warranted because of its cost, and, especially when just as sensitive, and cheaper units like thermistors are available. A photocell relay is unsuitable for temperature controllers other than the off-on types.

A temperature controller capable of controlling to at least $\pm 0.005^{\circ}\text{F}$, over a range from room temperature to 600°F , was designed and is shown schematically in Fig. 12. Although this controller was not completed in time to make its use possible in the reported work, test runs performed at a later date showed that it could control temperatures to the stated limits. The bath temperature will be controlled to $\pm 0.005^{\circ}\text{F}$ by a Wheatstone-bridge circuit, one leg of which is a thermistor suspended in the oil. A slight change in the temperature causes an unbalance



THERMISTOR - TYPE TEMPERATURE CONTROLLER

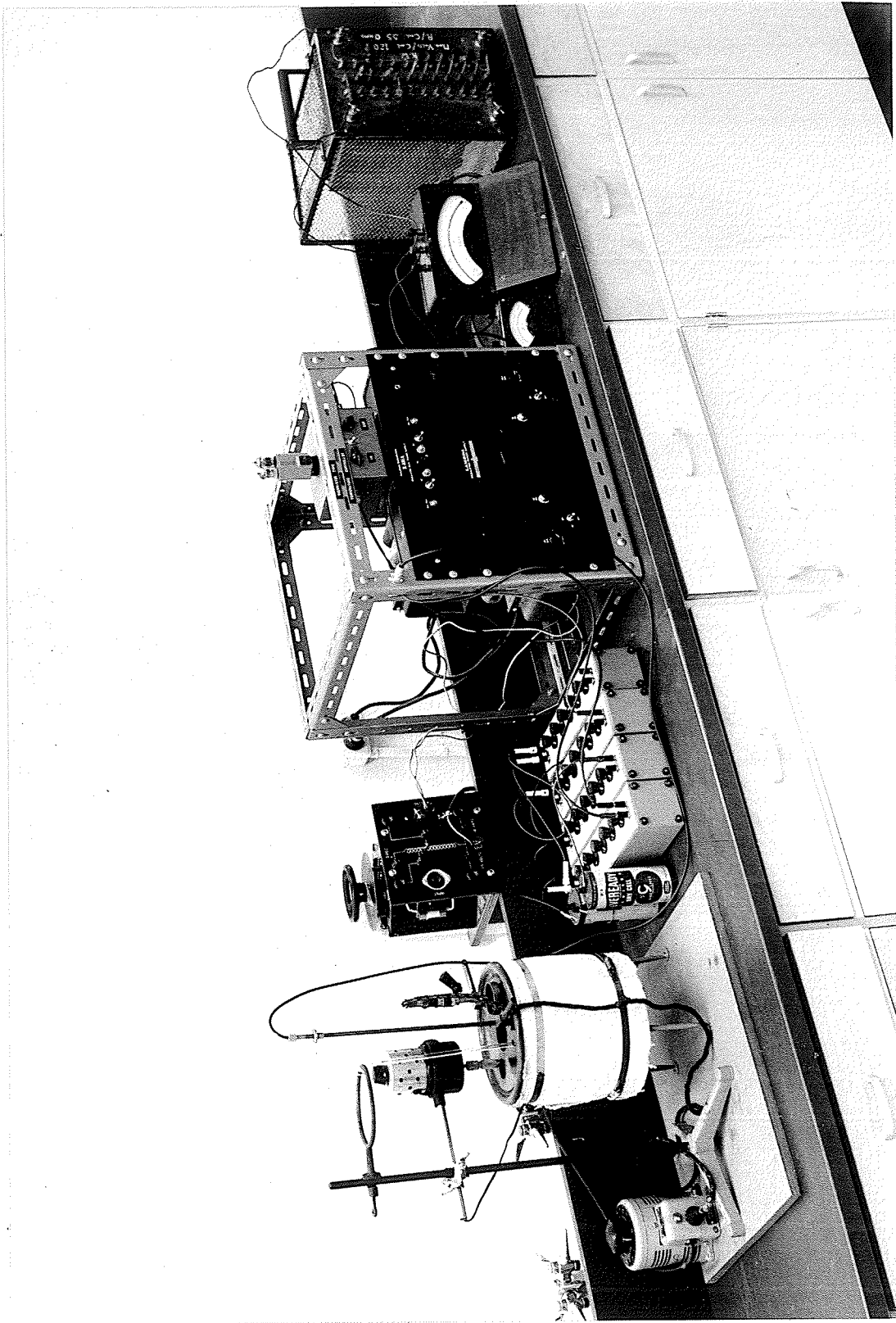
FIG.12.

in the bridge. The resulting error signal is amplified by an operational amplifier, and, it is then fed to a paralleled loss tube. The direct current being supplied to the control windings of the saturable-core reactor is changed in magnitude by the error signal, thus controlling the both heaters connected to the power windings of the reactor.

A thermistor was selected as the temperature sensing device because its resistance changes markedly with a slight change in temperature. A graph of the temperature-resistance relationship for the thermistor selected is shown in Appendix IV. Thermistors are "Thermal resistors" or resistors with a high negative temperature coefficient of resistance¹⁴¹, which is opposite to the effect of temperature changes on metals.

A thermistor bead was incorporated into a suitable temperature probe. The thermistor has a resistance of 100,000 Ohms at 77°F. When a particular temperature is to be controlled, the resistance of the thermistor at that temperature is obtained from the graph in Appendix IV, and the bridge circuit appropriately balanced. Three volts d.c. are supplied to the bridge, so that the resulting current is insufficient to cause any self-heating of the thermistor bead.

A slight change in temperature causes an unbalance in the bridge circuit. The resulting signal is amplified before it is fed to the loss tube. The output voltage, or the amplified error signal, is then fed to the grid of the paralleled 6AS7G loss tube. A regulated power supply is used to supply the required voltages to the loss tube, and the relevant electrical connections are shown in Fig. 12. The d.c. output



THEMISTOR-TYPE TEMPERATURE CONTROLLER UNDERGOING POST-ASSEMBLY TESTS

FIG. 13.

voltage from the loss tube is supplied to the control winding of a balanced saturable-core reactor³⁶, thus controlling the amount of a.c. voltage supplied to the bath heaters.

The operation of the designed temperature controller, therefore, is that when the bridge is balanced for a particular temperature a constant amount of d.c. voltage is being supplied by the loss tube to the control windings of the saturable-core reactor. When an unbalance occurs in the bridge circuit due to a change in the bath temperature, the voltage being supplied to the control windings of the saturable-core reactor increases or decreases, causing an increase or decrease, as the case maybe, in the alternating current being supplied to the bath heaters.

All the error signal transmitting leads are shielded co-axial cables - a precaution taken to avoid stray pick-ups.

Various characteristics of some of the components employed in the designed temperature controller are given in Appendix IV.

Fig. 13 shows a photograph of the thermistor-type temperature controller while it was undergoing post-assembly tests.

3. THE ARC WELDING APPARATUS

In general, there are the following six methods available for constructing a junction between two wires.

- (1) Mechanical contact, e.g. twisting the ends of the two dissimilar wires together.
- (2) Soldering or brazing.
- (3) Percussive welding.

- (4) Oxy-gas welding.
- (5) Resistance welding.
- (6) Arc welding.

Of the six methods possible, the arc welding method was selected since it was considered to be rather more convenient⁹⁴ for uniting two dissimilar wires which are laid side by side. The reasons for rejecting the other five methods are briefly as follows.

The mechanical contact method is of a temporary nature and the junction cannot be subjected to a high temperature.

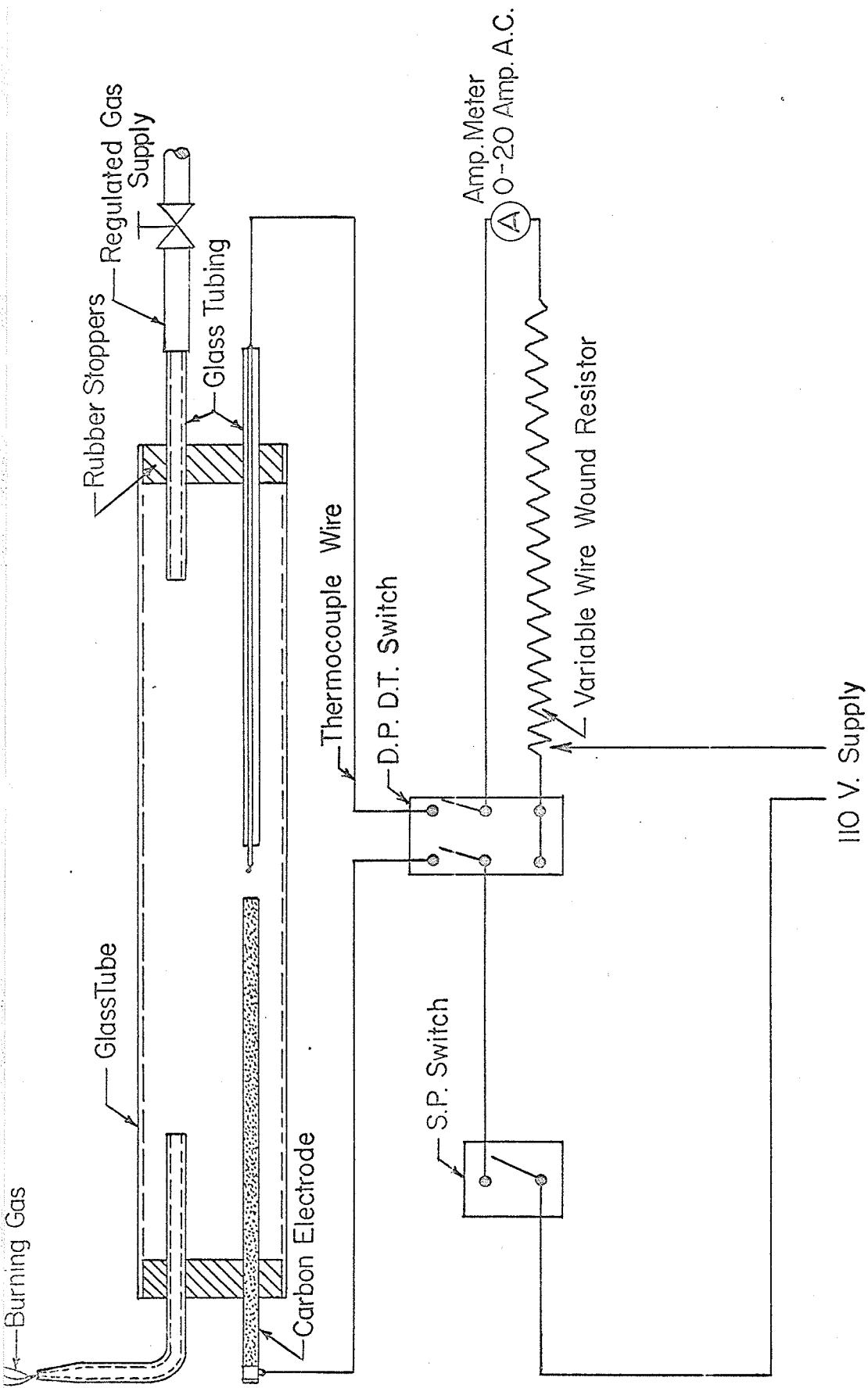
The soldering or brazing processes give thermocouples of reasonable performance, but the maximum temperature, to which the junction can be subjected is necessarily lower than that which the component metals will withstand, being determined by the melting point of the solder.

In the percussive welding process, a charged electrolytic condenser¹⁴⁸ is connected to the two clamped wires, one of which is approaching the other at high velocity; the discharge on contact affects the weld. However, the necessary equipment is of a rather specialized nature and quite expensive, but necessary for butt welding.

The oxy-gas welding process was rejected because it is unsuitable for small gauge wires and has a tendency to weaken the thermocouple wires just behind the bead.

The resistance welding is excellent for butt-welding thermocouples but arc welding process was selected because of its suitability for uniting wires which are laid side by side.

Fig. 14, shows the schematic diagram of the arc welding appara-



Schematic Diagram for Thermocouple Arc Welding Apparatus.

FIG.14.

tus used for welding thermocouples. This apparatus is a simplified version of that designed by the National Physical Laboratory⁶⁵, London.

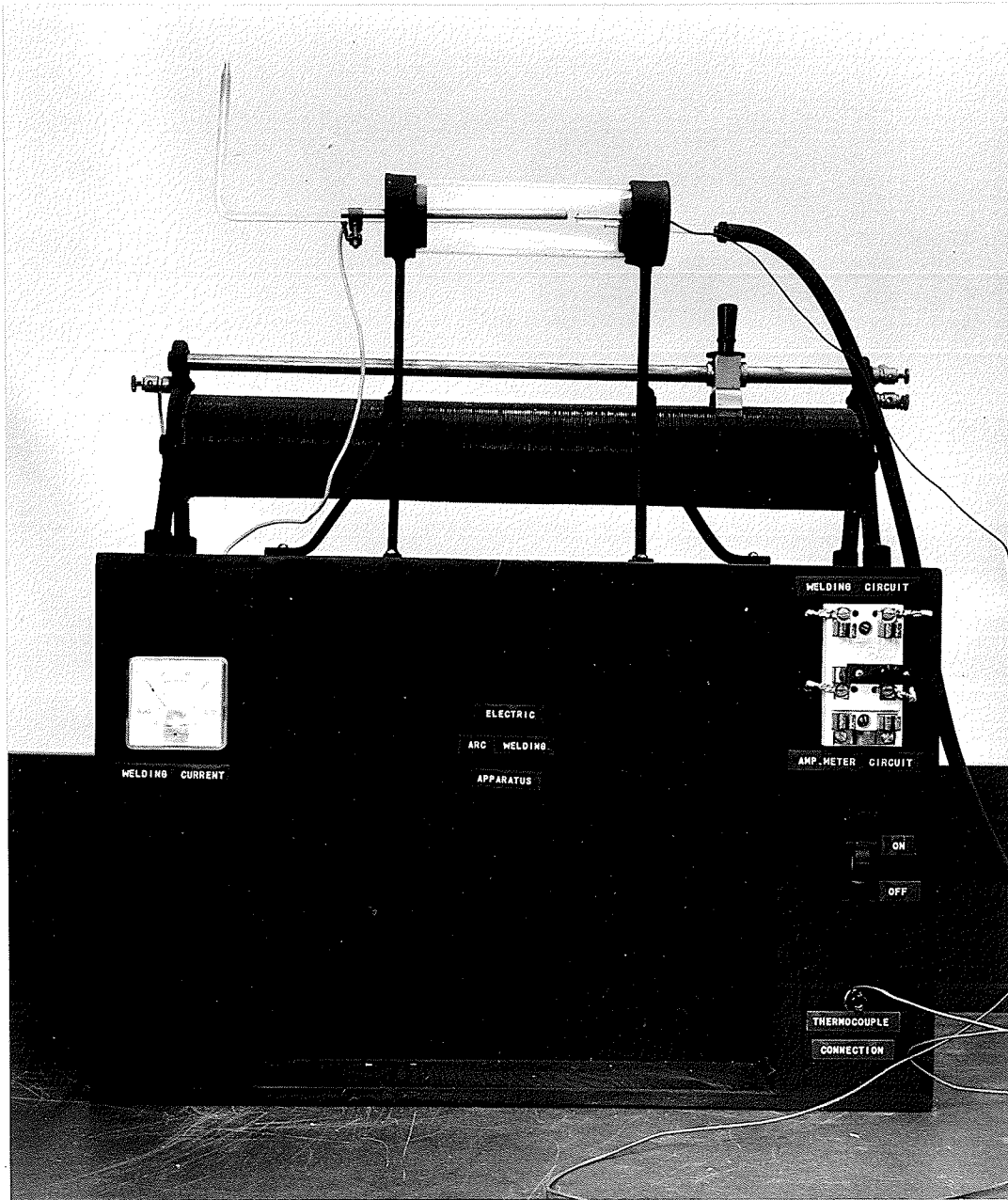
The apparatus consists of a Pyrex glass tube, 6 inches in length and 2 inches in outside diameter. A rubber stopper is inserted in each of the two open ends. Two $\frac{1}{4}$ inch diameter glass tubes are inserted in the main Pyrex glass tube through one of the rubber stoppers. One of these tubes is used for leading gas into the main tube while the other is used for leading in the thermocouple. Through the other rubber stopper, a $\frac{1}{4}$ inch diameter glass tube to let the gas flow out, and, a $\frac{1}{4}$ inch diameter carbon electrode, are inserted into the main tube. The graphite electrode is connected to one side of the supply mains.

The technique required for welding in this set-up is straight forward. Propane or hydrogen is led into the tube at one end and ignited at the other end. One end of each of the thermocouple wires is stripped, and they are twisted together, and, the end is nipped off. The further ends of both wires are connected to a terminal which leads through a variable resistance to the other side of the supply mains. The twisted end is then thrust through the glass tube provided for the thermocouple, and, allowed to touch the carbon electrode. As soon as the thermocouple completes the electrical circuit by touching the electrode, the twisted end is withdrawn about $\frac{1}{8}$ inch and the resulting arc forms a small bead bridging the ends of the wires. When the junction has cooled in the gas stream, it is withdrawn from the tube. This process is suitable for all the usual base metal thermocouples and can be used for pairs of wires of widely differing diameters.

The size of the bead can be controlled to some extent by adjustment of the current, and a provision in design of the electrical circuit has been provided to check the magnitude of the current before the arc welding operation is performed. The size of the bead can also be controlled by repeating the arcing several times. If the arcing is repeated it is desirable to clean the bead between each attempt.

The advantage of the thermocouple junctions made this way is that no fluxes are used, also the wire near the junction is not overheated and therefore not weakened as in flame welding. This method can be applied to a wide range of wire sizes, say from about 16 S.W.G. to 46 S.W.G. Tests on thermocouples made in this way have shown that the calibration of the thermocouple is unaffected.

A photographic view of the apparatus is shown in Fig. 15.



THE ARC WELDING APPARATUS

FIG. 15.

APPENDIX IVCHARACTERISTIC OF COMPONENTS EMPLOYED IN THE THERMISTOR-TYPE
TEMPERATURE CONTROLLER.(1) THERMISTOR TEMPERATURE PROBE.

The thermistor selected has the following characteristics:

Resistance at 77°F	:	100,000 ohms
Tolerance	:	± 2.5%
Code Number	:	GA 51 J 35
<u>Resistance at 77°F</u> <u>Resistance at 122°F</u>	:	10.3 (see graph for temperature and resistance relationship.)
Dissipation Constant	:	0.7
Time Constant	:	2 seconds
Lead Diameter	:	0.004 inch
Lead material	:	Platinum-Iridium
Lead length	:	0.25 inch
Thermistor bead diameter	:	0.043 inch
Manufacturer	:	Fenwal Electronics, Ind. Framingham, Massachusetts.

(2) OPERATIONAL AMPLIFIER

Model Number	:	M 2-X
Gain	:	300,000 d.c. open loop
Response	:	Small signal - 1 micro second rise time with band width over 250 KC when used as a unity - gain inverter.
Differential input levels	:	Impedance - either input - 100 M ohms (open grid)

Current : Either input - typically less than 10^{-8} ampere.

Bias required for balance : Adjustable from 0.8 to 1.8 volts between pin 1 and 2.

Power required for fuel output : Normal operation (100 K load) 11.8 milliamperes at + 300 volts d.c.
8.2 milliamperes at - 300 volts d.c.
0.75 ampere at 6.3 volts a.c. or volts d.c.

Tube complement : 1 12AX7 or 7025
1 6 AN 8

Temperature : Maximum allowable case temperature (hot spot) 149°F.

Base : Octal plus

Dimensions : Overall : 4.5 inches high
Above socket 1 7/16 inches wide. x
2 1/8 inches long x 4 3/32 inches high.

Manufacturer : George A. Philbrick Researchers, Inc.,
285 Columbus Avenue,
Boston 16, Massachusetts.

(3) LOSS TUBE-LOW MU TWIN TRIODE.

Tube Number : 6 A 57 - G

Base Connections : 8 BD

Filament Volts : 6.3

Filament amperes : 2.5

Maximum plate watts : 13 per section

Maximum plate volts : 250

Negative grid volts : $R_K=250$

Plate milliamperes : 125

R_p ohms : 280
 G_m , micro mhos : 7000
 factor : 2
 Manufacturer : Canadian General Electric Company.

(4) SATURABLE - CORE REACTOR

(a) Power Windings:

Maximum Voltage : 110 volts a.c. 60 cycles per second
 Rating : 1500 volts-amperes
 Maximum current
 at steady state : 14 amperes
 Windings tapped 0
 20
 40
 60
 80
 100 per cent turns.

If part of winding is used as primary, voltage must be pro-rated.

(b) Control Windings:

D.C. Resistance : 100 ohms
 Maximum current : 300 milliamperes d.c.
 Coil rated voltage : 100 volts d.c.

ELECTRONICS-THERMISTOR BEAD-CODE NO. GA 51J 35

GRAPH NO. 6.

