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ANOMALOUS SPECIFIC HEAT IN THE LIQUID PHASE

by

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## 1. INTRODUCTION AND SUMMARY OF PREVIOUS WORK

An extensive study of the physical properties of decahydronaphthalene has been made in the Chemical Engineering Laboratory at U.B.C. during the last ten years. The reasons for this study have been very well outlined by J.D. Leslie in his M.A.Sc. Thesis. (1). Decahydronaphthalene, or decalin, has been separated into two isomeric forms by vacuum distillation followed by repeated crystallizations. (2) The properties of the trans isomer have been found to be normal over the ranges studied but those of the cis isomer have shown a discontinuity around  $50^{\circ}\text{C}$ , similar to those of liquid helium at the  $\Lambda$  point of  $2.2^{\circ}\text{K}$ . For this reason it has been suggested that the cis isomer may have a second order phase transition around  $50^{\circ}\text{C}$ .

A comparison of the properties of cis decalin around  $50^{\circ}\text{C}$  with those of liquid helium at the  $\Lambda$  point of  $2.2^{\circ}\text{K}$  are given below, and are contrasted, where possible, with those of a normal substance at a first order phase transition point.

### (1) Variation of Partial Pressure with Temperature

If the logarithm of the partial pressure is plotted against the reciprocal of the absolute temperature, the following curves for liquid helium and cis decalin are obtained.

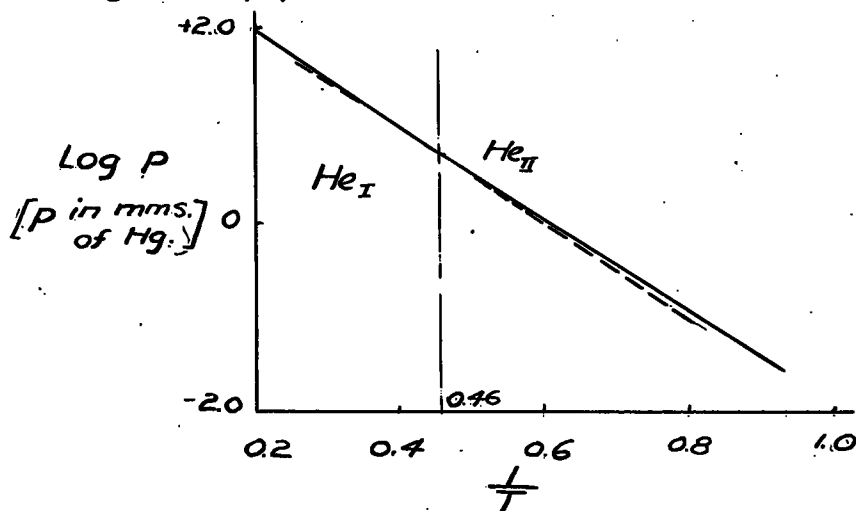
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(1) J.D. Leslie, M.A.Sc. Thesis, 1941.

(2) Angley, Potkins, and Rush, B.A.Sc. Thesis, 1942.

(a) Liquid helium at  $\lambda$  point of  $2.2^\circ \text{ K}$  (1)

Figure 1 (a)

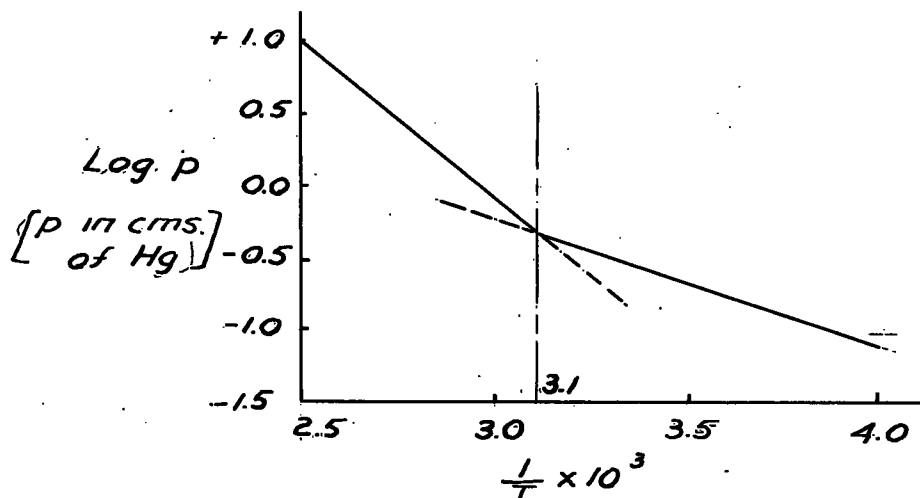


The slope of the logarithm of the partial pressure curve changes at the transition point.

(b) Cis decalin at  $50^\circ \text{ C}$

(2)

Figure 1 (b)



The slope of the logarithm of the partial pressure curve changes at  $50^\circ \text{ C}$ .

(1) "Phenomena at the Temperature of Liquid Helium"

E.F. Burton, H. Grayson Smith, & J.O. Williams pp.68

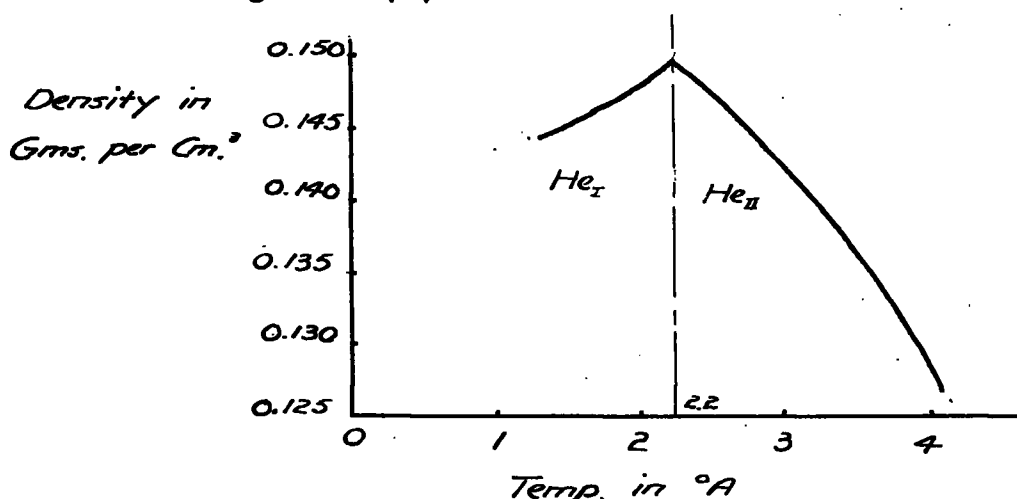
(2) C.W.J. Mann, M.A.Sc. Thesis, 1944.

## (2) Variation of Density with Temperature

The graphs below show the variation of the density with temperature of liquid helium at the  $\Lambda$  point, cis decalin at  $50^\circ \text{C}$ , and a substance undergoing a first order phase transition change, eg, water boiling.

### (a) Liquid helium at the $\Lambda$ point (1)

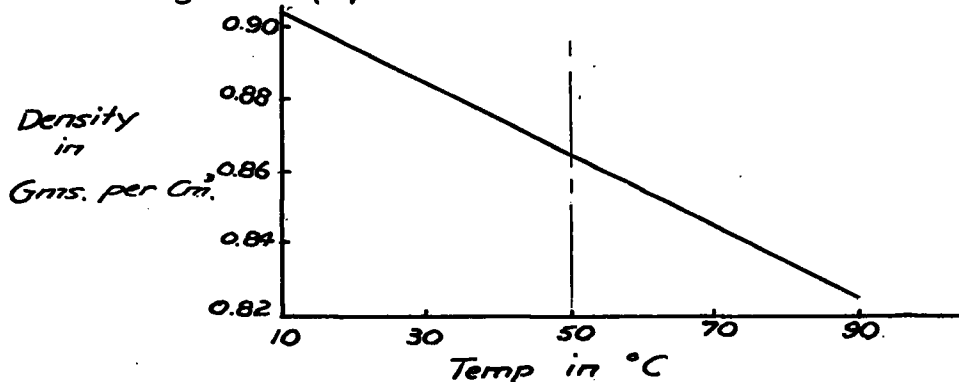
Figure 2 (a)



The density undergoes no change at  $2.2^\circ \text{K}$  but the slope of the curve changes.

### (b) Cis decalin at $50^\circ \text{C}$ . (2)

Figure 2 (b)



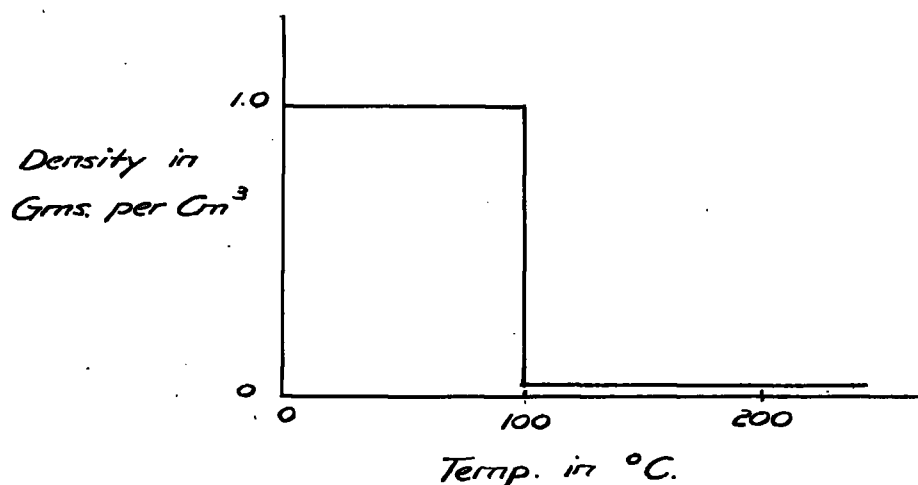
- 
- (1) E.F.Burton, H.Grayson, Smith, J.O.Wilhelm, Op.cit., pp.69  
 (2) C.A.Davenport, M.A.Sc. Thesis, 1938



There is no change in the density or any appreciable change in the slope of density curve at  $50^{\circ}\text{C}$

(c) Water to steam at  $100^{\circ}\text{C}$

Figure 2 (c)



An abrupt change in the density occurs in a first order phase transition.

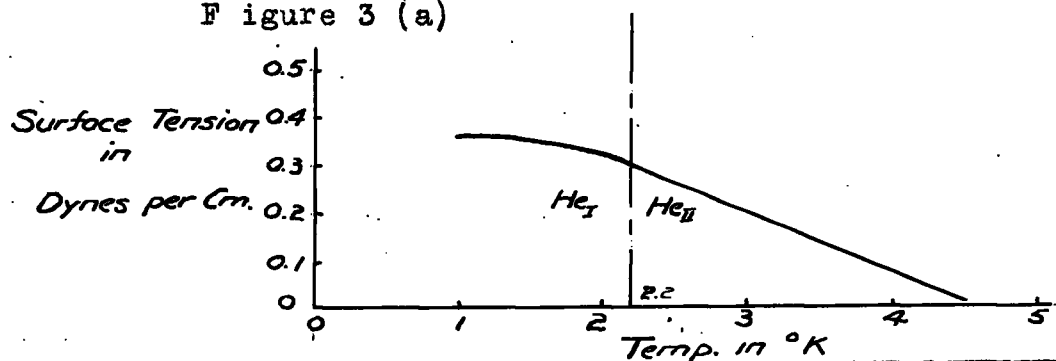
### (3) Variation of Surface Tension with Temperature

On plotting the surface tension against the temperature, the following curves are obtained for helium at the  $\lambda$  point, and cis decalin at  $50^{\circ}\text{C}$ .

(a) Liquid helium at  $2.2^{\circ}\text{K}$

(1)

Figure 3 (a)

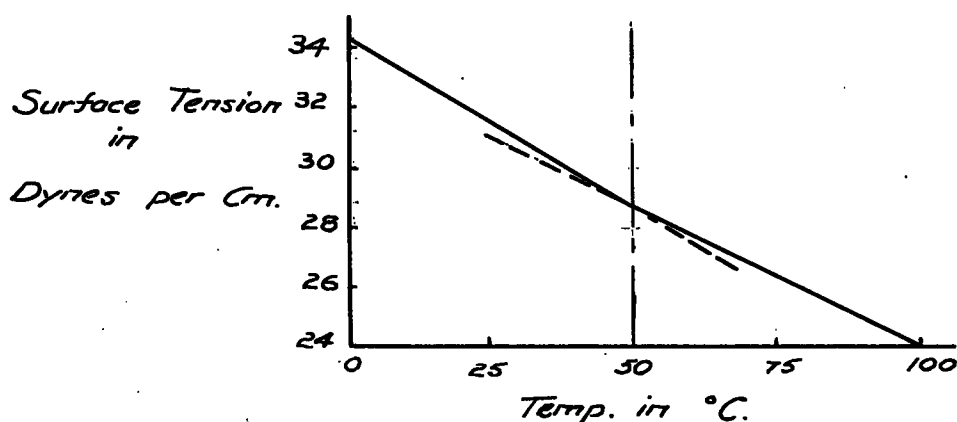


(1) E.F.Burton, H.Grayson Smith, J.O.Wilhelm, op.cit., pp 76

The surface tension experiences no change at the  $\Lambda$  point, but the slope of the surface tension curve changes.

(b) Cis decalin at  $50^{\circ}\text{C}$  (1)

Figure 3 (b)



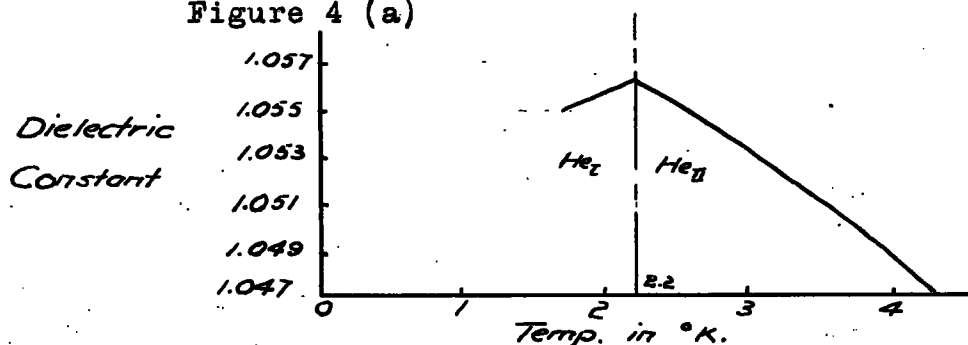
Cis decalin, also, shows no change in the surface tension at  $50^{\circ}$  but the slope of the surface tension curve changes.

(4) Variation of the Dielectric Constant with Temperature

The graphs shown below give the change of the dielectric constants with temperature of liquid helium and cis decalin,

(a) Liquid helium at  $2.2^{\circ}\text{K}$  (2)

Figure 4 (a)



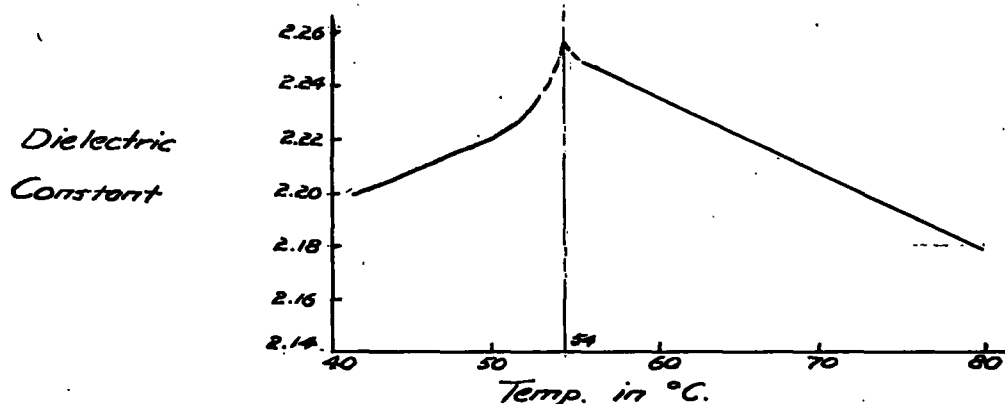
(1) C.A.Davenport, M.A.Sc. Thesis, 1938

(2) E.F. Burton, H.Grayson Smith, J.O. Wilhelm, op.cit., pp 77

The dielectric constant does not change at  $2.2^{\circ}\text{K}$  although the slope of the dielectric constant curve changes rather abruptly.

(b) Cis Decalin at  $50^{\circ}\text{C}$  (1)

Figure 4 (b)



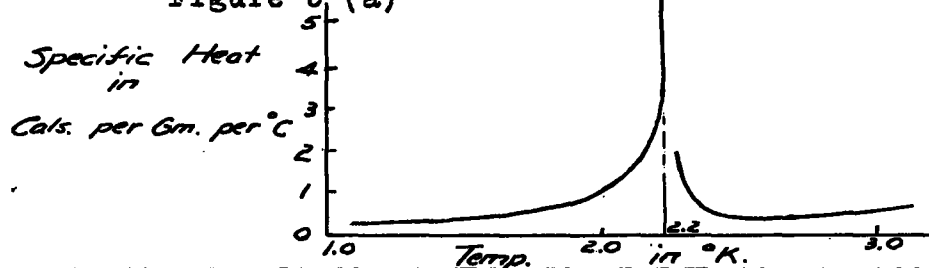
The curve for cis decalin around  $50^{\circ}\text{C}$  is very similar to that for liquid helium at  $2.2^{\circ}\text{K}$ .

(5) Variation of Specific Heat with Temperature

On plotting the specific heat against temperature the following curves for liquid helium at the  $\lambda$  point and cis decalin around  $50^{\circ}\text{C}$  are obtained. These graphs are contrasted with that of a substance undergoing a first order phase transition, eg, water boiling.

(a) Liquid helium at  $2.2^{\circ}\text{K}$  (2)

Figure 5 (a)

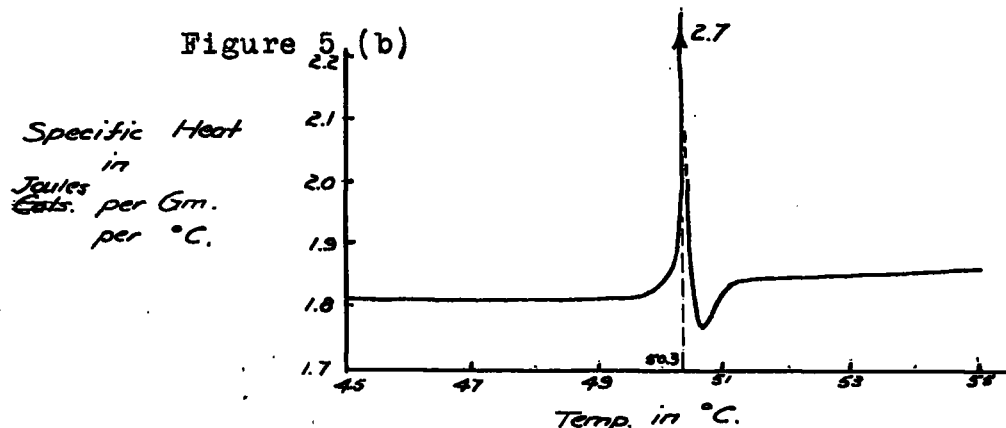


(1) B.A.Dunell, Masters Thesis, 1946.

(2) E.F.Burton, H.Grayson Smith, J.O.Wilhelm, op. cit., pp 75

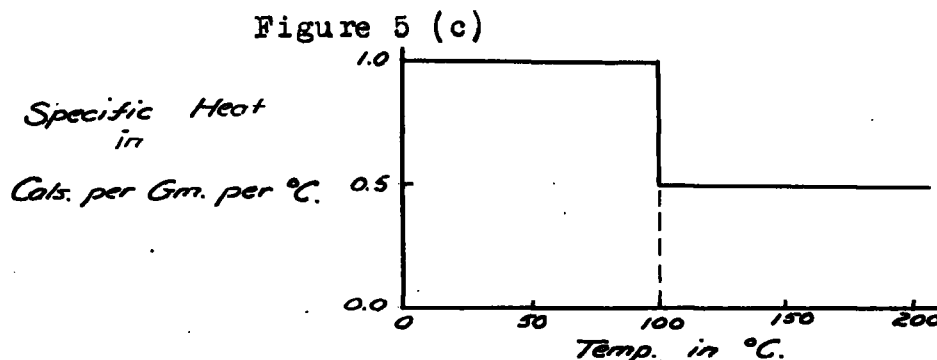
The specific heat curve shows a marked discontinuity at the  $\wedge$  point but the specific heat and the slope of the curve are nearly the same before and after the break.

(b) Cis Decalin around  $50^{\circ}$  C determined by Miss Robinson (1) using the Isothermal Method.



The above curve for cis decalin shows a marked resemblance with that of liquid helium at the  $\wedge$  point. It should be noted, however, that previous investigators G.F. Davies (2), D.E. McLellan, (3), and H.M. Graham (4) when using the adiabatic method obtained a wavy specific heat curve over the region concerned.

(c) Water to steam at  $100^{\circ}$  C.



- 
- (1) M. Robinson, M.A. Thesis, 1945.
  - (2) G.F. Davies, M.A.Sc. Thesis, 1932.
  - (3) D.E. McLellan, M.A.Sc. Thesis, 1943.
  - (4) H.M. Graham, M.A.Sc. Thesis, 1944.

An abrupt change in the specific heat occurs during the above first order phase transition and the specific heat before and after the transition are not the same.

As a conclusion from the previous experimental data, it seems apparent that cis decalin exhibits anomalous behaviour around  $50^{\circ}$  C and shows indications of having a second-order phase transition in this region.

## 2. OBJECT OF THE RESEARCH

The chief aim of this research was to try to confirm the results, made by previous investigators, of the specific heat of cis decalin. In particular, the anomalous change of the specific heat with temperature around  $50^{\circ}$  C was to be investigated by the isothermal method. It was decided to use temperature differences of the order of one-tenth of a degree to quantitatively determine the shape of the specific heat-temperature curve around the indicated second-order phase transition point, and from the graph to determine the change in enthalpy or heat content at this point.

## 3. METHODS FOR MEASURING THE SPECIFIC HEAT OF LIQUIDS

The Adiabatic and the Isothermal Methods.

In both methods a measured amount of heat is added to a weighed amount of the substance in question, and the rise of temperature is observed.

## (a) ADIABATIC METHOD of J.W. Williams and F. Daniels (1)

In the adiabatic calorimeter, the substance concerned is placed in a container and is surrounded by a bath liquid. The temperatures of substance and the region surrounding it are maintained the same throughout an adiabatic specific heat measurement. The specific heat is then given by the formula,  $S = \frac{Q}{(\Delta \theta)(w)}$  where  $Q$  is the heat added,

$\Delta \theta$  is the observed rise of temperature

$w$  is the weight of the substance.

Since the temperatures of the substance and the region surrounding it are the same, there is no heat loss by conduction and radiation. The adiabatic method, however, was not found satisfactory to find the specific heat in small temperature ranges and hence was not used in this research.

## (b) ISOTHERMAL METHOD of W.P. White (2)

In the isothermal method the substance in question is placed in a container surrounded by a bath liquid. With this method, however, the substance in the container is not maintained at the same temperature as that of the surrounding bath. If the substance is hotter or colder than the region around it, it will lose or gain heat respectively by conduction and radiation. When heat is added to the substance it will

- 
- (1) Williams J.W., & Daniels F., "The Specific Heats of Certain Organic Liquids at Elevated Temperatures", J.A.C.S. vol. 46, pps. 303-317, 1924.  
 (2) White W.P., "Some Calorimetric Methods", the Phys. Review Vol. 31, pp. 545-48, 1910.

experience a rise in temperature, but this rise will not be the rise which would have resulted without heat transfer to or from the jacket. For the isothermal method, then, a correction for the transfer of heat must be applied to the formula given for the adiabatic type of determination.

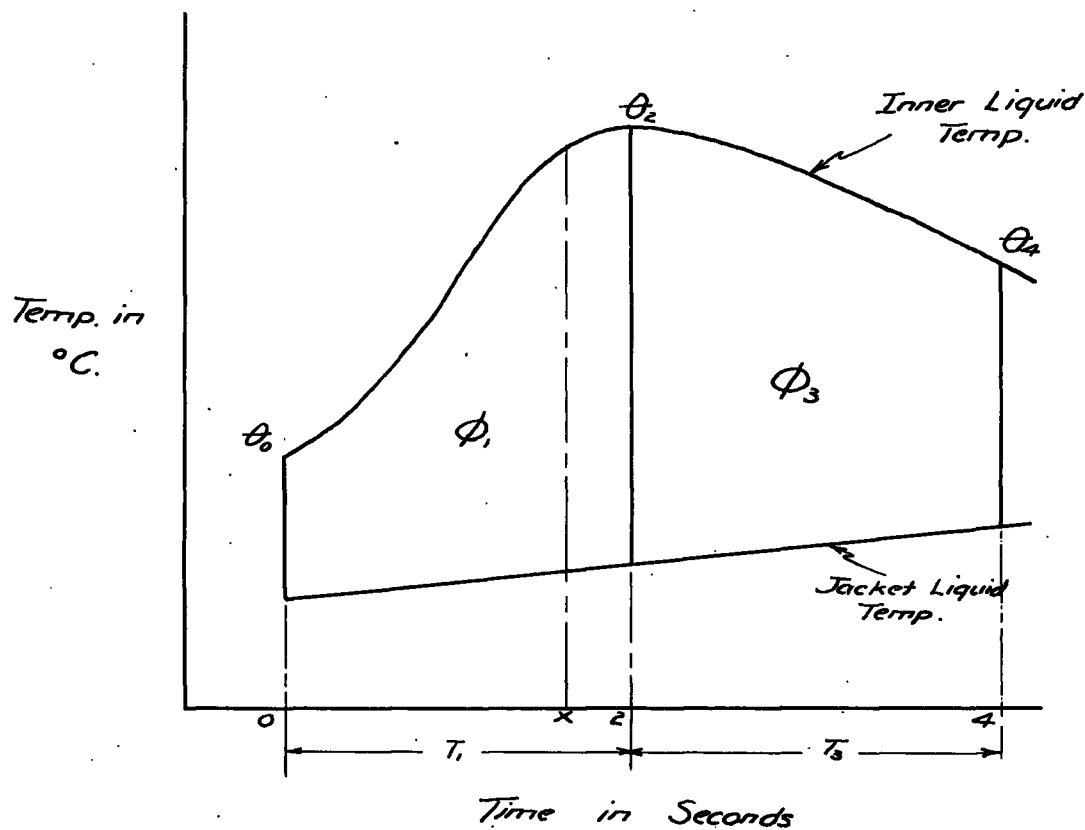
The isothermal method depends for its accuracy on the method used for determining the heat transfer correction mentioned above. Since the substance in the container ~~is~~ usually hotter than the liquid of the jacket, heat is lost to the liquid, and the increase in temperature of the substance <sup>is</sup> not as great as it would be if no heat were lost by it. The heat transfer equation then is usually a cooling correction.

The method for determining the cooling correction used in this research is the one described by W.P. White. (1) Suppose that the container, holding a liquid whose specific heat is to be measured, is immersed in a jacket liquid with both liquids adequately stirred so that no temperature gradients exist within them. Then a measured amount of heat is added to the liquid in the container and the temperature of this liquid is measured as the heat is being added. Similarly when the inner liquid is cooling by losing heat to the jacket liquid, the temperature of the inner liquid is measured again. Then on plotting a graph with temperatures as ordinates and times as abscissa, a cooling curve is obtained as follows

---

(1) Ibid.

Figure 6.



At time 0 the addition of heat is started.

At time  $x$  the addition of heat is stopped.

But the temperature of the liquid continued to rise because of lags in the heating devices.

At time 2 the temperature reaches a maximum.

Time 4 is any time later.

Now let:

$\theta_0$  be the inner liquid temperature at time 0.

$\theta_2$  be the inner liquid temperature at time 2, etc.

Also let:

$T_1$  be the time interval from 0 to 2.



$T_3$  be the time interval from 2 to 4.

$\phi$  be the temperature difference between the inner liquid and the jacket liquid at time  $T$ .

$\omega$  be the temperature fall per minute due to the combined effect of evaporation and stirring.

$\phi_m$  be  $\int_m \phi dT$  where  $m$  stands for any time interval  $T_m$ .

It is apparent that  $\phi_m$  equals the area bounded by the two liquid temperature curves and the two abscissa forming the boundaries of the time interval  $T_m$ .

The heat  $dQ$  lost in any element of time  $dT$  during the experiment because the inner liquid is hotter than the jacket liquid is given by:

$$dQ = C \phi dT \dots\dots\dots(1)$$

where  $C$  is a constant.

This statement assumes that Newton's Law of cooling holds, that is, it assumes that the rate of loss of heat is proportional to the temperature difference between the two liquids. Then in any period of time  $T_m$  the total amount of heat lost is

$$\int_m dQ = \int_m C \phi dT$$

or

$$Q_m = C \int_m \phi dT = C \phi_m \dots (2)$$

Thus the total amount of heat lost by the inner to the jacket liquid during a time interval is proportional to the area bounded on the left and right by the boundaries of the time interval and on the top and bottom by the two liquid temperature curves.

Now consider the time interval  $T_3$

The total loss of temperature by the liquid is given by  $\theta_2 - \theta_4$

The loss of temperature caused by the combined effects of evaporation and stirring by  $\omega T_3$

Call the loss of temperature caused only by the difference in temperature of the jacket and container liquids the direct temperature loss. Then the direct loss in the interval  $T_3$  is  $(\theta_2 - \theta_4) - \omega T_3$  .... (3)

Now let:

$Q_1$  be the direct heat loss in period 1

$Q_3$  be the direct heat loss in period 3

Then from the above discussion in Equation (2)

$$Q_1 = C \phi_1$$

$$Q_3 = C \phi_3$$

$$\text{or } \frac{Q_1}{Q_3} = \frac{\phi_1}{\phi_3} \quad \dots (4)$$

Now let:

$Q_1'$  be the direct temperature loss in period 1

$Q_3'$  be the direct temperature loss in period 2

Then because

$$\frac{Q_1'}{Q_3'} = \frac{Q_1}{Q_3} \quad \dots (5)$$

it is true that

$$\frac{Q_1'}{Q_3'} = \frac{\phi_1}{\phi_3} \quad \dots (6)$$

Now by Equation (3)

$$Q_1' = \theta_2 - \theta_4 - \omega T_3 \quad \dots (7)$$

Then by Equation (6) the direct temperature loss in period (1) is given by

$$Q_1' = \frac{Q_3'}{Q_3} (\theta_2 - \theta_4 - \omega T_3) \quad \dots (8)$$

Then the total loss of temperature in the period  $T_1$  is given by

$$\eta = \frac{\phi_1}{\phi_3} (\theta_2 - \theta_4 - \omega T_3) + \omega T_1 \quad (9)$$

and this expression is the cooling correction desired, and this correction is added to the observed rise in temperature. The result is  $\Delta\theta$  which may be substituted in the expression

$$S = \frac{Q}{(\Delta\theta)(\omega)}$$

which was the formula used to find the specific heat in the adiabatic discussion.

To make Equation (9) more convenient to use, some rearrangements should be made. Replacing  $\frac{\phi_1}{\phi_3}$  by  $\frac{\phi_3 + \phi_1 - \phi_3}{\phi_3}$  or  $1 + \frac{\phi_1 - \phi_3}{\phi_3}$ , Equation (9) becomes

$$\begin{aligned} \eta &= \left(1 + \frac{\phi_1 - \phi_3}{\phi_3}\right) (\theta_2 - \theta_4 - \omega T_3) + \omega T_1 \\ &= \theta_2 - \theta_4 + \left(\frac{\phi_1 - \phi_3}{\phi_3}\right) (\theta_2 - \theta_4 - \omega T_3) + \omega (T_1 - T_3) \quad (10) \end{aligned}$$

In this research the time intervals  $T_1$  and  $T_3$  were made of the same length so that the fourth term of Equation (10) vanishes. The areas  $\phi_1$  and  $\phi_3$  were determined from the graph by a polar planimeter. For reasons to be given later  $\omega$  was taken as zero. Hence the simplified equation used in this research to determine the temperature cooling correction was  $\eta = \theta_2 - \theta_4 + \frac{\phi_1 - \phi_3}{\phi_3} (\theta_2 - \theta_4) \dots (11)$

#### 4. APPARATUS.

##### (a) The Calorimeter

The calorimeter is similar to that of Williams and Daniels (1) and is the same one used here by previous workers. It is very adequately described and illustrated

(1) Williams J.F. and Daniels F., op.cit.pp.303/317.

by D.E.McLellan in his M.A.Sc. Thesis. (2) Several modifications that have been made on the calorimeter<sup>since</sup> this work was published, are listed below.

Miss M. Robinson in 1945 added a lead weight to the bottom of the cup container to reduce its buoyancy in the glycerin bath and thus preventing excess pressure on the cup stirrer. She added 5% water to the glycerin bath to reduce its high viscosity around 25° C, and inserted two three-bladed propellers to stir this bath. She also inserted a variable transformer of the type 100-Q to manually control the electrolytic A.C. heating of glycerin bath.

In this research a 500 volt knife heater was added for rapid heating of the glycerin bath. One of the 3 bladed stirrers in conjunction with the electrolytic heating kept the bath temperature constant throughout. The maximum deviation between the temperatures of the bath was found by a platinum resistance thermometer to be 0.01° C.

(b) Apparatus for Measuring Temperatures and Energy Input.

(1) The temperature of the glycerin bath was measured by a platinum resistance thermometer and a Muller Bridge.

(2) The temperature difference between the cup and the bath were measured by a rive junction thermopile made from Leeds and Northrup insulated copper-constantin thermocouple wire. The reason why the new thermopile was used is given

under the section on "Calibration of Equipment."

(3) In order to get consecutive measurements, of the E.M.F. produced by the thermopile and the power input to the cup heater, on a Universal Type K Potentiometer, the wiring system was rearranged and is shown in the following diagram

The E.M.F. of the thermopile was read by adjusting the potentiometer to give zero deflection on a galvanometer.

The electrical energy to the cup heater was taken from a 120 ampere hour storage battery, and was controlled by a resistance box. The dummy resistance, whose resistance was nearly the same as the heater circuit, was used to discharge the initial high voltage of the battery before starting an experiment. The voltage drop across the heater was measured on the potentiometer, the voltage first being reduced to a measurable quantity through a volt box. The current was determined by measuring the voltage drop across a standard ohm. In both cases the voltage was read from the potentiometer when galvanometer gave a zero deflection.

Figure 7. Diagram for Measuring Power Input to the Cup Heater and Thermopile Reading

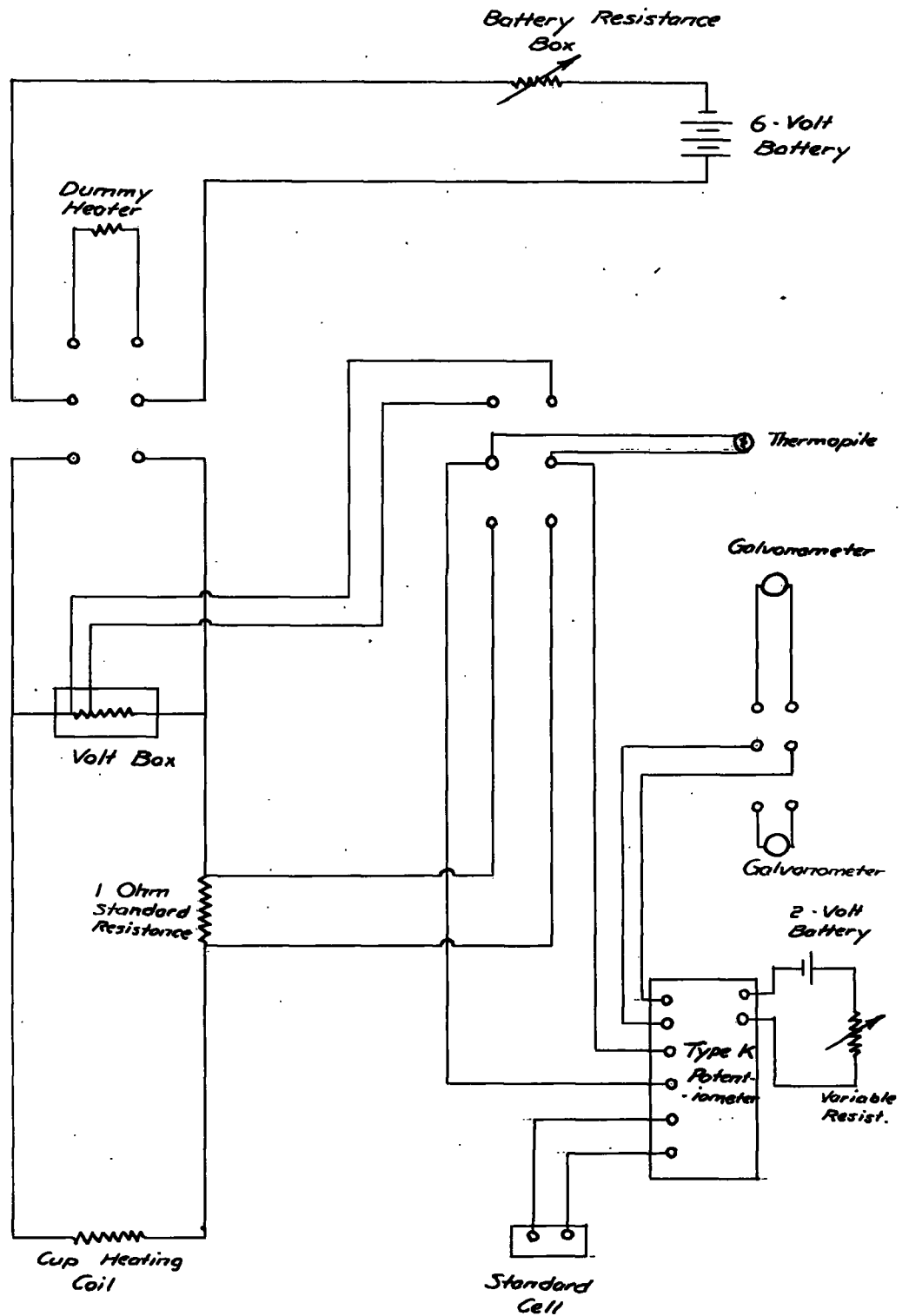
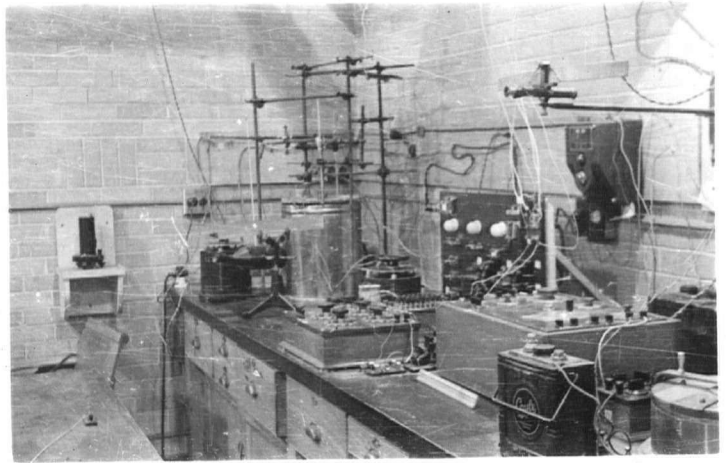
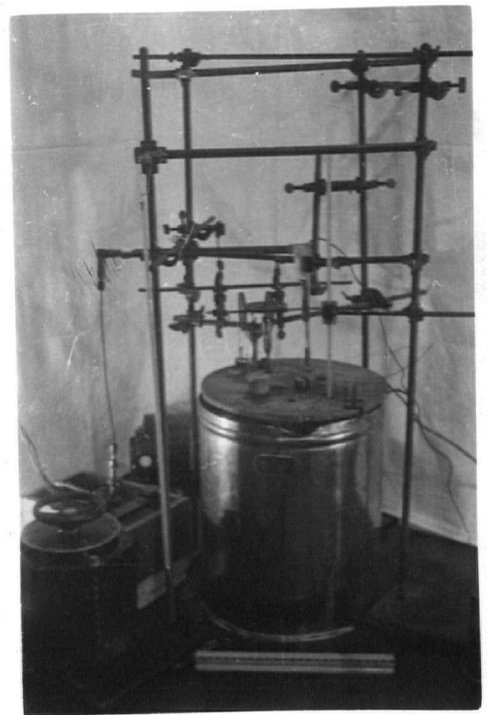


Figure 8.

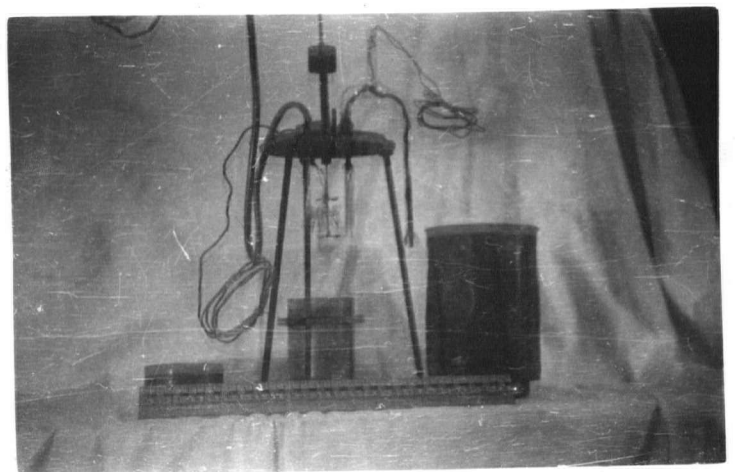
(a) *The Apparatus  
as a whole*



(b) *The Calorimeter  
Container*



(c) *The Calorimeter  
and the  
Thermopile*



## 5. MATERIALS USED

### (a) Cis Decalin.

Cis decalin was separated from a mixture of the cis and trans isomers by rectifying the mixture at 9 mm. absolute pressure in a Stedman Column (1). The purest fraction of the cis isomer so produced had a purity from 99.5-99.8%. This fraction of the cis decalin was further purified by several crystallizations in a dry ice bath, following the method used by Seyer and Walker (2). The final product had a constant freezing point of  $43.13^{\circ}\text{C}$ , as measured by a Platinum resistance thermometer. The refractive index measured on a Pulfricht Refractometer was *1.48116*

### (b) Benzene & Toluene

Merc."thiopine free" benzene and toluene were used to determine the water equivalent of the calorimeter.

## 6. CALIBRATION OF THE APPARATUS

### (a) The Thermopile.

#### (1) Required Accuracy.

The temperature of the bath could be read to  $0.01^{\circ}\text{C}$  on the platinum resistance thermometer used in conjunction with a Muller Bridge and could be estimated to  $0.001^{\circ}\text{C}$  by the calibration of a galvanometer scale. The power input to the cup could be measured by the type K potentiometer to five significant figures. Hence it follows, to carry this

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(1) Angley, Potkins and Rush, B.A.Sc. Thesis, 1942.

(2) Seyer and Walker J.A.C.S. 60 2125, (1938).

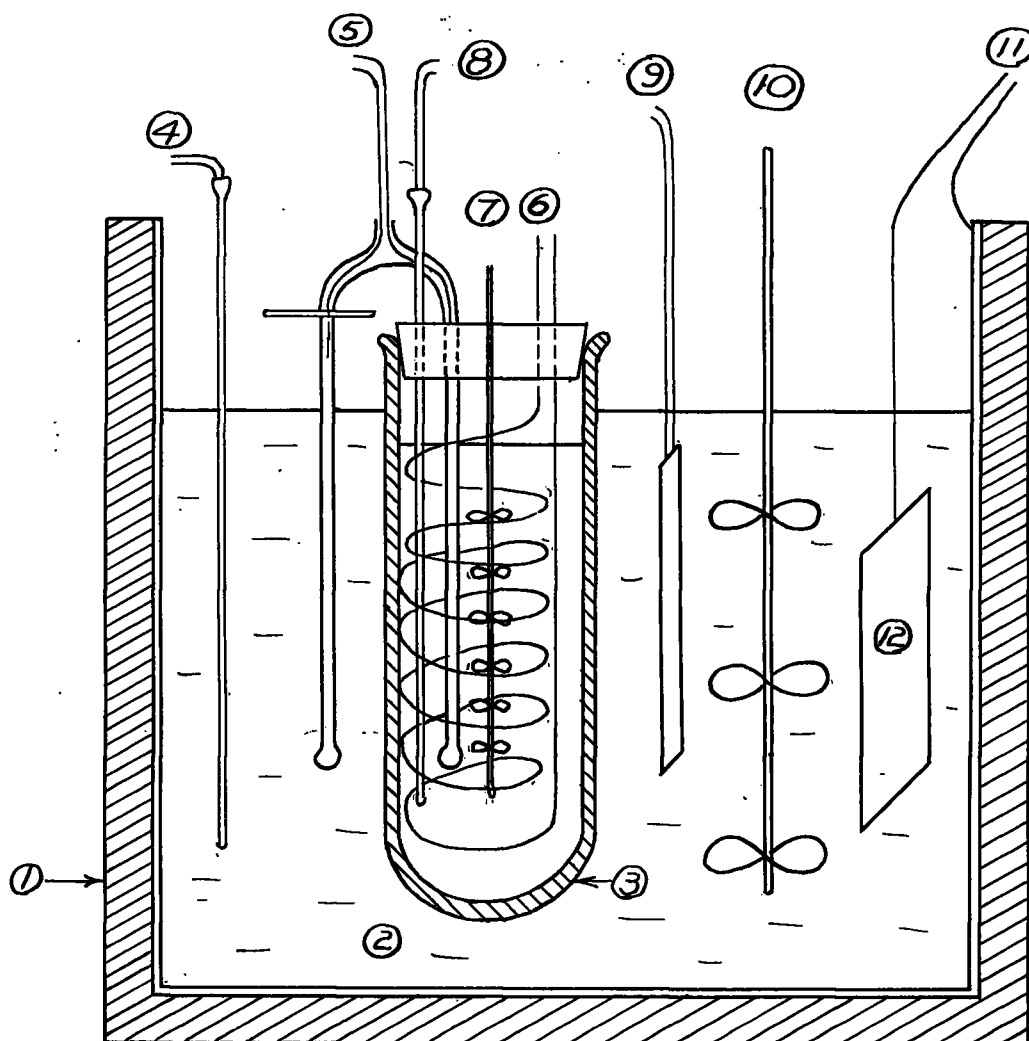


five figure accuracy throughout, the thermopile must be calibrated to give five figure accuracy.

(2) Method of Thermopile calibration

The thermopile was calibrated using the apparatus shown in the following diagram.

Figure 9



1. Cylindrical copper container lagged with cotton.
2. Glycerine bath
3. Dewar flask containing trans decalin
- 4 & 8 Platinum resistance thermometers connected to Muller  
Bridges with galvanometers and scale.
5. Thermopile with leads going to type K potentiometer.
6. Nicrome resistance heater for heating the Dewar flask.
7. Stirrer for Dewar flask.
9. 500 Volt knife heater
10. Stirrer for outer bath.
11. Leads to A.C. source to supply electrolytic heat to the  
bath.
12. Copper plate, of same surface area as the calorimeter  
cup, to act as an electrode for the electrolytic  
heating.

In the calibration of the thermopile, the glycerine bath was heated to a few degrees above the trans decalin bath, the temperatures of both baths were evened out, and simultaneous readings of the temperatures of the outer and inner baths, and the E.M.F. produced by the thermopile were taken.

The following table was made from the results obtained by the thermopile used by Miss Robinson (1)

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(1) M. Robinson, op. cit., 1945.

TABLE #1

Reading No.	Temp. of bath °C	Temp. of Dewar Flask °C	Difference in Temp. °C	Mean Temp °C	Voltage Generated <i>μV</i>	Voltage/ Degree <i>μV/°C</i>
1.	26.909	22.997	3.312	24.953	751.3	192.0
2.	31.563	27.968	3.595	29.766	723.3	201.2
3.	37.860	34.220	3.640	36.040	819.3	225.1
4.	43.061	39.418	3.643	41.240	838.5	230.2
5.	55.374	52.368	3.606	54.171	926.7	257.0
6.	48.552	45.713	2.839	47.132	724.7	255.3
7.	52.800	45.542	3.258	51.171	844.5	259.2
8.	80.705	76.570	4.135	78.638	1215.5	294.0
9.	69.195	65.659	3.536	67.427	1003.2	283.7
10.	62.705	58.651	4.054	60.678	1077.0	265.7
11.	31.238	28.905	2.333	30.072	515.4	220.9
12.	26.403	22.306	4.097	24.354	703.5	171.7
13.	26.526	21.633	4.893	24.080	854.1	174.6
14.	32.159	28.130	4.029	30.144	798.7	198.2
15.	39.144	35.316	3.828	37.230	892.4	233.1
16.	45.411	41.051	4.360	43.231	1043.9	239.4
17.	51.953	47.569	4.384	49.711	1104.9	252.0
18.	57.214	53.085	4.129	55.150	1091.2	264.3
19.	34.581	33.471	1.108	34.027	322.0	290.6
20.	35.872	33.528	2.344	34.700	573.5	244.7
21.	37.150	33.588	3.572	35.374	815.3	228.2
22.	39.300	33.698	5.602	36.499	1230.3	219.6
23.	39.250	38.361	0.289	39.106	179.6	621.4
24.	39.240	38.861	0.379	39.051	220.5	581.8
25.	39.240	38.771	0.469	39.006	247.3	527.3

From the data given in table (1) it appeared that the thermopile behaved very irregularly, but seemed to suggest the magnitude of the temperature difference between the legs of the thermopile had a great effect on the voltage generated. This effect was shown to be true by decreasing the temperature difference between the legs of the thermopile and is illustrated in the table. and graph below.

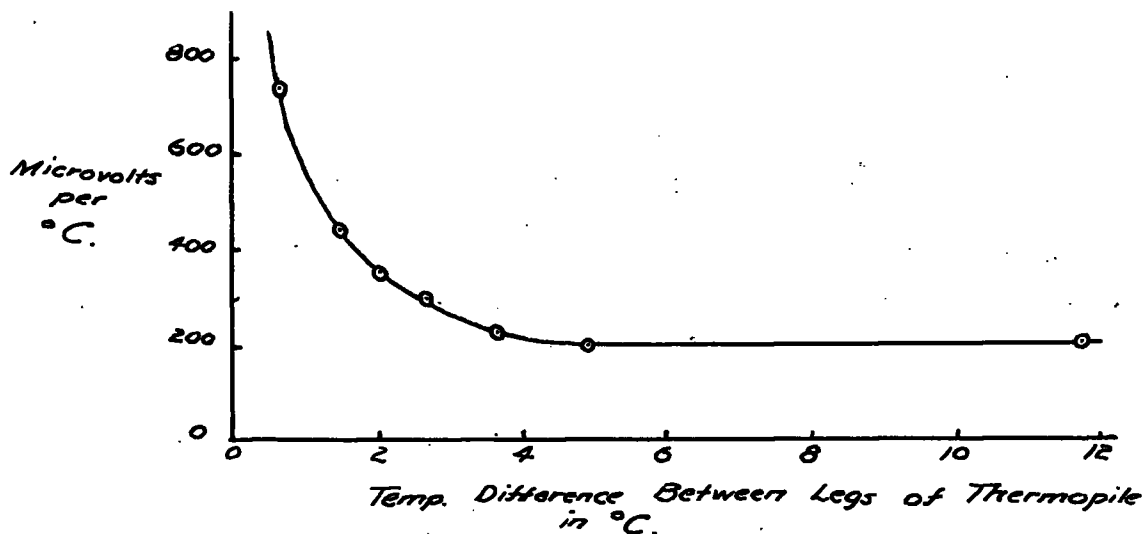
TABLE 2

Reading No	Temp of Bath in °C	Temp of Dewar Cup in °C	Diff in Temp. in °C	Mean Temp in °C	Volt Generated <i>μV</i>	Volt / Degree <i>μV/°C</i>
1.	39.023	27.702	11.327	33.366	2072	182.9
2.	39.144	34.485	4.659	36.814	974	208.1
3.	39.204	35.548	3.656	37.376	909	248.6
4.	39.224	36.516	2.708	37.870	763	281.8
5.	39.254	37.388	1.866	38.321	648	347.3
6.	39.294	37.997	1.297	38.645	576	444.1
7.	39.314	38.680	0.634	38.997	468	738.2

Figure 10

The Variation of E.M.F. per °C with the temperature difference between the thermopile legs of the Copper-Copel Thermopile .

Figure 10.



This thermopile would give very erratic results in the temperature range of  $0.1^{\circ}\text{C}$  between the cup and bath temperatures and hence was discarded.

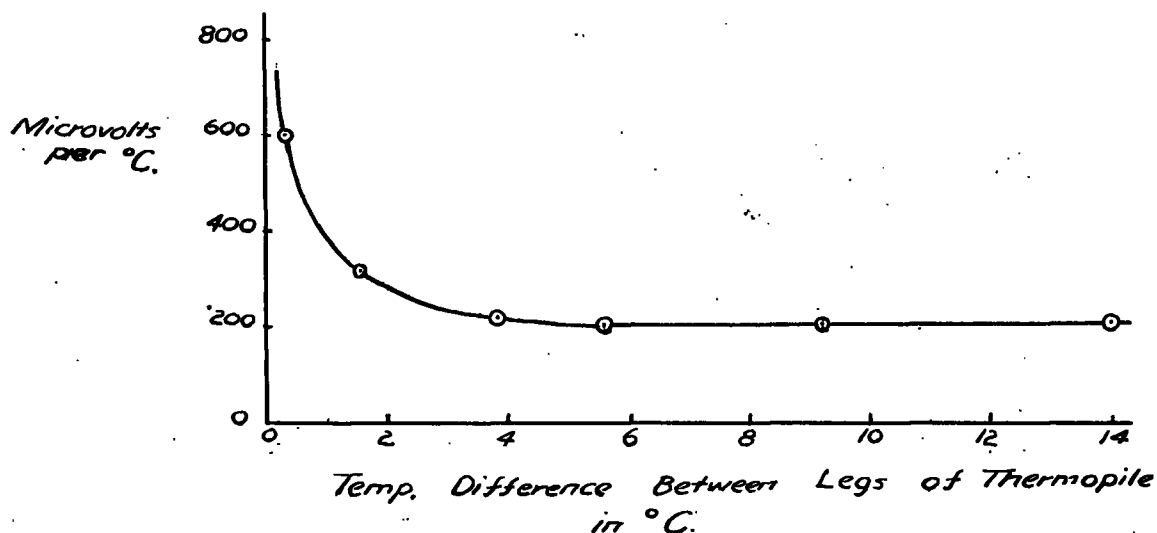
A new five junction copper-constantin thermopile was made up from insulated Leeds and Northrup thermocouple wire. The thermopile was tested similarly to the one described above, and the results proved as erratic. The following table and graph illustrate this.

TABLE 3

Reading No.	Temp. of Bath in $^{\circ}\text{C}$ .	Temp. of Dewar Cup in $^{\circ}\text{C}$ .	Diff. in Temp. in $^{\circ}\text{C}$ .	Mean Temp. in $^{\circ}\text{C}$ .	Volt. Generated per $^{\circ}\text{C}$ $\mu\text{V}$	Volt. per $^{\circ}\text{C}$
1	39.232	24.973	14.259	32.102	2621.6	183.86
2	39.295	30.112	9.183	34.686	1869.4	203.57
3	39.335	34.018	5.317	36.677	1172.3	220.48
4	39.355	35.795	3.560	37.575	845.0	237.36
5	39.355	38.037	1.398	38.696	422.3	302.07
6	39.385	38.990	0.395	39.188	238.3	603.29

Figure 11

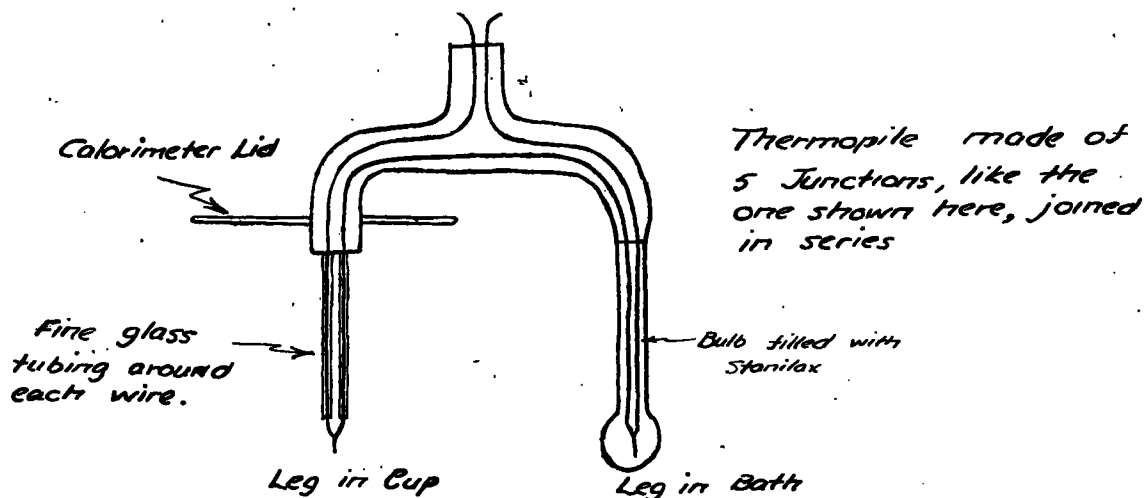
Variation of E.M.F. per Degree with Temperature Difference between Legs of Copper-Constantin Thermopile.



It was decided that the lag in the heat transfer through the glass bulb and stanilax in the bulb surrounding the thermopile leg caused an infinite time to be required for the thermopile to acquire the cup. temperature. To eliminate this lag the glass bulb was removed from around the thermopile and direct contact between the bath liquid and the thermopile resulted. The thermopile wires were spaced and separated from each other by fine glass tubes as shown in Figure 11. As the glycerine bath temperature remained very nearby constant throughout a run the lag would not affect the thermopile leg in it. The glass bulb was left on this leg otherwise the electrolytic bath would influence the thermopile readings.

Figure 12

Construction of Copper Constantin Thermopile to  
Reduce Heating Lags



The thermopile calibration was checked with those given for Copper-Constantin in Leeds and Northrup Thermocouple tables P.41. With one leg of the thermopile in crushed ice made from distilled water and the other in distilled water the following readings were made.

TABLE 4.

E.M.F. Produced by Thermopile <i>in <math>\mu V</math></i>	Water Temp. in $^{\circ}C$	$\mu V/^{\circ}C$
4245.7	21.30	200
4224.8	21.00	200.5
4088.8	20.60	198.6

These results check with the value of  $200 \mu V/^{\circ}C$  found in the table for a five junction copper-constantin thermopile and this calibration was taken as correct.

## (b) Water Equivalent of Calorimeter.

Eight isothermal runs were made with "Merc." toluene to determine the water equivalent of the calorimeter. The procedure was the same as that described later to determine the specific heat of cis decalin and a Leeds and Northrup Potentiometer #553553 was used to measure the E.M.F. produced by the thermocouple. A sample calculation is given below.

## Water Equivalent Run #4.

Average bath temperature	= 21.20° C
Resistance of the leads	= 0.17902 ohms
Mean temperature of the cup	= 21.76° C
(1) Specific heat of toluene at 21.76	= 1.671 Joules/ gm./°C
Total heating time	= 685.5 seconds
<u>To determine the total heat input</u>	
Voltage drop through the heat <sup>α</sup> circuit	
= (0.042605) (50)	= 2.13025 V.
Current through the heater	= 0.27076 a.
Voltage drop across the leads	
= (0.27076) (0.17902)	= 0.04847 v
Voltage drop across the standard ohm.	
= (0.27076) (1)	= 0.27076 V
Voltage drop across heater	
= (2.13025 - 0.04847 - 0.27076)	= 1.81102 V
Heat input per second.	
= (1.81102) (0.27076)	= 0.490352 Watts



Total heat input

$$H = (0.490352) (685.5) = 336.14 \text{ Joules}$$

To determine the total temperature rise

$$\eta = \theta_2 - \theta_1 + (\theta_2 - \theta_1) \left( \frac{\phi_1 - \phi_3}{\phi_1} \right)$$

$\theta_1$  and  $\theta_2$  were taken from the graph

$\phi_1$  and  $\phi_3$  were measured from the graph by a polar planimeter.

$$\eta = 1.115 - 0.828 + (1.115 - 0.828) \left( \frac{599 - 925}{599} \right) = 0.186^\circ\text{C}$$

Total temperature rise

$$\Delta\theta = \theta_2 - \theta_1 + \eta$$

$$= 1.115 - 0 + 0.186 = 1.301^\circ\text{C}$$

To determine the water equivalent

$$\Delta\theta(Q) = H - (W \times S \times \Delta\theta)$$

$$\text{where } \Delta\theta = \text{total temperature rise} = 1.301^\circ\text{C}$$

$$W = \text{weight of toluene} = 140.23 \text{ g}$$

$$S = \text{specific heat of toluene} = 1.671$$

$$\therefore Q = \frac{336.14 - (140.23) (1.671) (1.301)}{1.301}$$

$$= 24.04 \text{ joules} / ^\circ\text{C}$$

A summary of the water equivalents of the calorimeter is given below in Table 5.

TABLE 5

Run No.	Mean Temp. of Toluene	Water equivalent of Calorimeter in Joules /°C
1	19.08	19.48
2	19.85	30.16
3	21.68	22.87
4	21.74	24.04
5	21.12	21.32
6	22.84	26.29
7	24.42	27.63
8	24.61	34.13

At an average temperature of 21.92° C the average water equivalent is 25.74 Joules /° C. This mean result was considered satisfactory because any errors are magnified by having to subtract two quantities of the order of 300 to get one of the order of 25. The increase of the water equivalent per degree was found to be 0.1 joules for 10° C on the basis of a water equivalent of 38 joules /° C at 30° C (1).

The increase for this calorimeter is

$$\frac{25.75}{38.0} \left( \frac{1}{10} \right) (0.1) = 0.007 \text{ joules } /^{\circ}\text{C}/^{\circ}\text{C}$$

(c) The Heat of Stirring and Evaporation

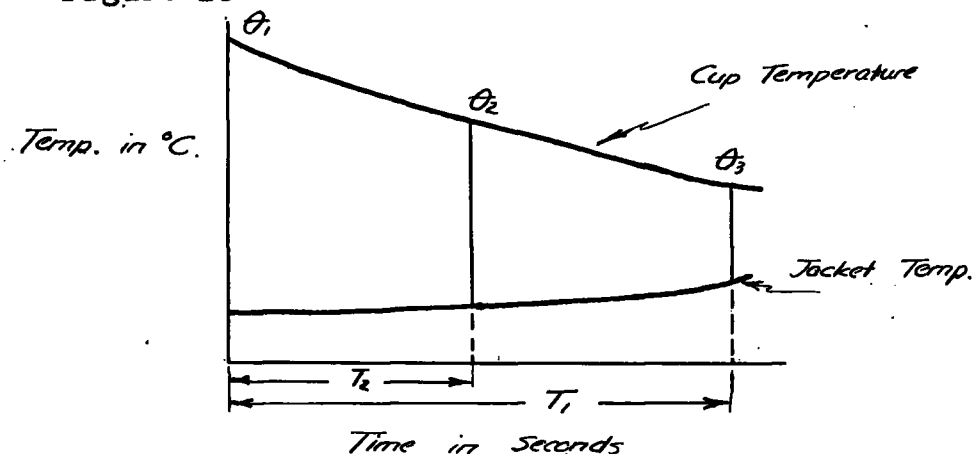
To determine the heat of stirring and evaporation,  $\omega$ , the cup containing the cis decalin was allowed to cool while being stirred with no heat supplied. A graph as

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(1) D.E.McLellan, M.A.Sc. Thesis, 1943.

shown in figure 13 was obtained.

Figure 13



Then the direct loss of temperature in time  $T_1$

$$= \theta_1 - \theta_2 - \omega T_1$$

$$\text{in time } T_2 = \theta_1 - \theta_3 - \omega T_2$$

But as shown before on page 13

The direct temperature loss in  $T_1$  is  $\propto \Phi_1$

The direct temperature loss in  $T_2$  is  $\propto \Phi_2$

Thus

$$\frac{\text{Direct loss in } T_1}{\text{Direct loss in } T_2} = \frac{\Phi_1}{\Phi_2}$$

$$\text{Therefore } \theta_1 - \theta_3 - \omega T_1 = \frac{\Phi_1}{\Phi_2} (\theta_1 - \theta_2 - \omega T_2)$$

And  $\omega$  can be solved from this equation as all other terms are known. As shown on page 35 for the graph of Cis Decalin run #28 the results needed to calculate the heat of stirring are as follows:

$$\theta_1 = 0.1996, \quad \theta_3 = 0.1520, \quad \theta_2 = 0.1781$$

$$\Phi_1 = 1650, \quad \Phi_2 = 746$$

$$T_1 = 17.7 \text{ min.}, \quad T_2 = 7.3 \text{ minutes}$$

$$\therefore 0.1996 - 0.1520 - \omega (17.7) = \frac{1650}{746} (0.1996 - 0.1781 - \omega \times 7.3)$$

and  $\omega = 0.00003$  °C/minute.

In a similar manner the heat of stirring was found in three other runs and the results are given in Table 6.

TABLE 6.

Cis Decalin Specific Heat Run No.	Heat of Stirring °C/minute.
28	0.00003
29	0.0003
30	-0.0007
32	-0.0005

The result concluded is that the heat of stirring and evaporation is either very small positively or negatively and will, in later considerations, be taken as zero.

#### 7. PROCEDURE FOR DETERMINING THE SPECIFIC HEAT OF CIS DECALIN

Runs 1 - 18 inclusive were made by adding sufficient heat to raise the temperature of the cis decalin in the cup by about  $1.5^{\circ}$  C. Runs 18 - 36 inclusive were made by adding enough heat to raise the cis decalin temperature from  $0.1$  to  $0.2^{\circ}$  C. The purpose of the first 18 runs was to check the results with those of previous investigators from  $20 - 50^{\circ}$  C. There a few runs were to be taken from  $20 - 50^{\circ}$  C using the smaller temperature interval; if these results agreed with those made in the first runs, the method would be satisfactory to explore around the anomaly in the specific heat curve at

50-50.5° C.

The procedure used in both cases was very similar. In the first set of runs the glycerine bath and the cis decalin<sup>if</sup> the cup were brought to some desired temperature, both baths were stirred and temperatures maintained constant for approximately 15 minutes before starting a run. Then a measured amount of power was added to the nicrome heater in the cis decalin for about 900 seconds. Then the power was shut off and the cup was allowed to cool for an equal length of time. The temperature of the glycerine bath was read continuously in both periods by the platinum Resistance Thermometer #317863, and the E.M.F. of the thermopile by Leeds and Northrup Potentiometer #634358.

In the second set of runs the temperatures were maintained constant for about 1/3 - 1 hour before starting the run. The E.M.F. of the thermopile was read by the Type K Universal Potentiometer.

A typical set of results is given in table 7 for cis decalin run #28

TABLE 7

Time in Seconds	Potentiometer Reading in $\mu V$	Temp. Diff. from Bath to Cup $^{\circ}C$	Power-Input Volt. Current Volts Amps.	Bath Temp. in $^{\circ}C$
0	11.15	0.0558		34.531
127	14.4	0.072		
155				34.528
192	16.5	0.0825		
213				34.529
273				34.528
406				34.527
439			0.676475	
478				34.528
561			0.085778	
592				34.528
687				34.529
735				34.529
830				34.530
885	35.05	0.1752		
913	36.5	0.1825		
967	37.85	0.1892		
986				34.529
1030			POWER OFF	
1037	39.4	0.1970		
1062	39.6	0.198		34.529
1097	39.45	0.1972		
1144	39.4	0.196		

Time in Seconds	Potentiometer Reading in <i>mV</i>	Temp. Diff. from Bath cup °C	Power-Input Voltage Current Volts Amps	Bath Temp in °C
1145				34.529
1227				34.528
1256	37.85	0.1892		
1388	36.45	0.1822		
1425				34.530
1563	34.4	0.172		
1662				34.530
1690	33.05	0.1652		
1800				34.531
1869				34.530
1902	31.35	0.1568		
1957				34.530
2020	30.5	0.1525		
2049				34.523
2093	30.1	0.1505		
2154				34.530
2196	29.55	0.1478		

From table 7, figure 14 was drawn for cis decalin run #28.

#### 8. SAMPLE CALCULATION of SPECIFIC HEAT of CIS DECALIN

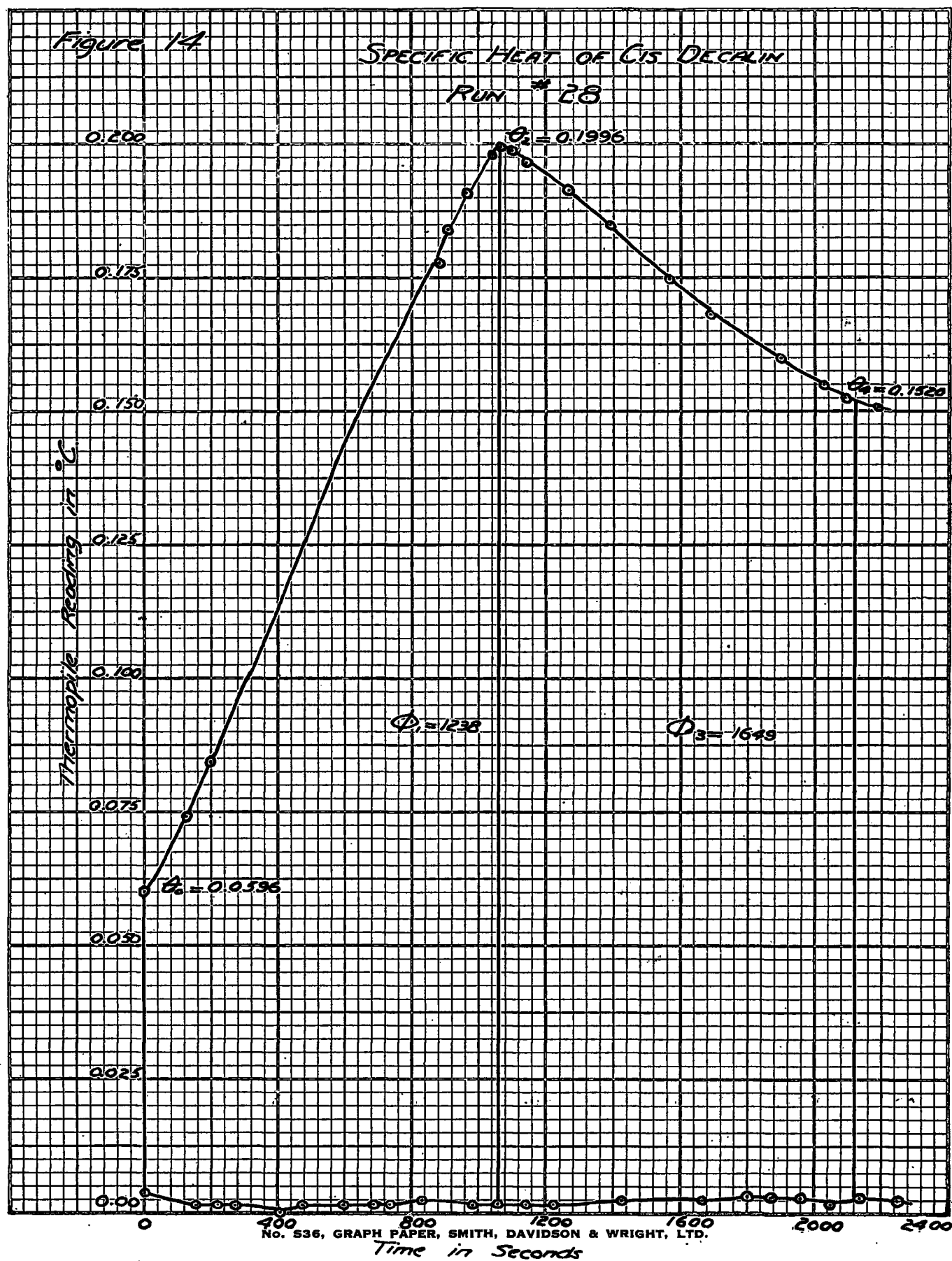
-from the data of Table 7 and figure 14.

##### (a) Determining Power Input

Voltage drop across heater circuit = 0.676475 V

Figure 14

SPECIFIC HEAT OF CIS DECALIN  
RUN #28





Current through the heater circuit = 0.085778 a

Voltage drop across leads.

$$= (0.085778) (0.17988) = 0.015430 \text{ V}$$

Voltage drop across standard ohm = 0.085778

Voltage drop across heater

$$= (0.676475 - 0.015430 - 0.085778) = 0.575267 \text{ V}$$

Heat input per second

$$= (0.575267) (0.085778) = 0.049346 \text{ Watts}$$

Total heat input

$$H = (0.049346) (1030) = 50.826 \text{ Joules}$$

(b) Determining the Total Temperature Rise.

$$\eta = \theta_2 - \theta_4 + (\theta_2 - \theta_4) \left( \frac{\phi_1 - \phi_3}{\phi_3} \right)$$

From figure 14.

$$\theta_2 = 0.1996 \quad \theta_4 = 0.1520$$

$$\phi_1 = 1238 \quad \phi_3 = 1649$$

$$\eta = 0.1996 - 0.1520 + (0.1996 - 0.1520) \left( \frac{1238 - 1649}{1649} \right)$$

$$= 0.0357 \text{ } ^\circ\text{C}$$

Total temperature rise

$$= \theta_2 - \theta_4 + \eta$$

$$= 0.1996 - 0.0596 + 0.0357$$

$$= 0.1757 \text{ } ^\circ\text{C}.$$

(c) Determining the Specific Heat of Cis Decalin

$$(W)(\Delta\theta)(S) = H - (\Delta\theta)(\text{Water Equivalent})$$

where

$$W = \text{weight of cis decalin} = 146.64 \text{ g}$$

$$\Delta\theta = \text{total temperature rise} = 0.1757 \text{ } ^\circ\text{C}$$

$$S = \text{specific heat of decalin}$$

$H$  = heat input = 50.826 Joules

Water Equivalent = 25.83  $\frac{\text{Joules}}{^{\circ}\text{C}}$

$S$  = 1.7961 Joules per gram, per degree.

## 9. RESULTS

The specific heat of cis decalin from 20-50  $^{\circ}\text{C}$  <sup>is</sup> ~~was~~ given in Table 8 for the runs 1-18 inclusive.

TABLE 8

Run No.	Avg. Decalin Temperature in $^{\circ}\text{C}$	Total Temp Rise of Decalin in $^{\circ}\text{C}$	Specific Heat Joules /gm/ $^{\circ}\text{C}$
1	21.52	1.4716	1.8135
2	27.03	1.5102	1.8021
3	32.66	1.6154	1.7992
4	37.58	1.5185	1.7430
5	25.08	1.6973	1.8191
6	43.67	1.5783	1.7731
7	48.82	1.5931	1.7970
8	28.42	1.5847	1.7999
9	35.64	1.6900	1.8123
10	23.80	1.7674	1.8148
11	30.17	1.3916	1.7902
12	36.78	1.2241	1.8131
13	40.79	1.3800	1.8090
14.	39.72	1.2980	1.8321
15	40.51	1.3720	1.8306
16	43.36	1.3004	1.8218

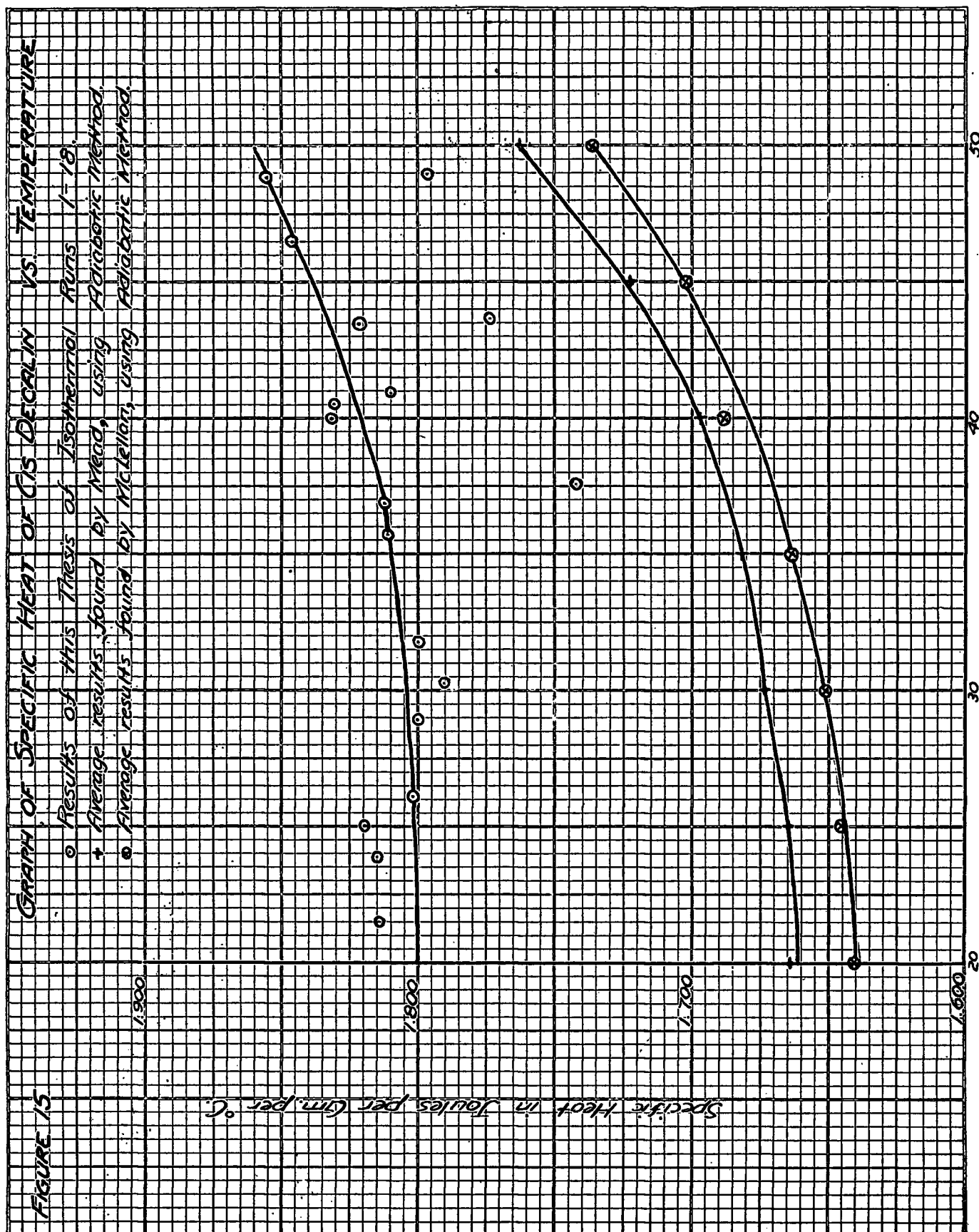
Run No.	Avg. Decalin Temperature in °C	Total Temp Rise of Decalin in °C	Specific Heat of Decalin in Joules /gm/°C
17	46.50	1.2457	1.8457
18	48.68	1.2666	1.8565

The specific heat-temperature curve for cis decalin between 20°-50°C found by runs 1-18 inclusive is shown in figure 15. For comparison, the results of Mead and McLellan are shown between the same temperature limits.

The results obtained for the specific heat of cis decalin from runs 18-36 inclusive are given in table 9.

TABLE 9

Run No.	Avg. Decalin Temperature in °C	Total Temp of Decalin in °C	Specific Heat of Decalin in Joules /gm/°C
19	48.774	0.1502	1.5914
20	Results discarded as battery Connection loose.		
21	48.109	0.1628	1.8987
22	49.602	0.2052	1.9030
23	35.829	0.1928	1.7568
24	49.992	0.2071	1.8311
25	50.123	0.1761	1.6443
26	50.202	0.1825	1.7892
27	30.089	0.1969	1.7391
28	34.657	0.1757	1.7361
29	40.068	0.1871	1.6050



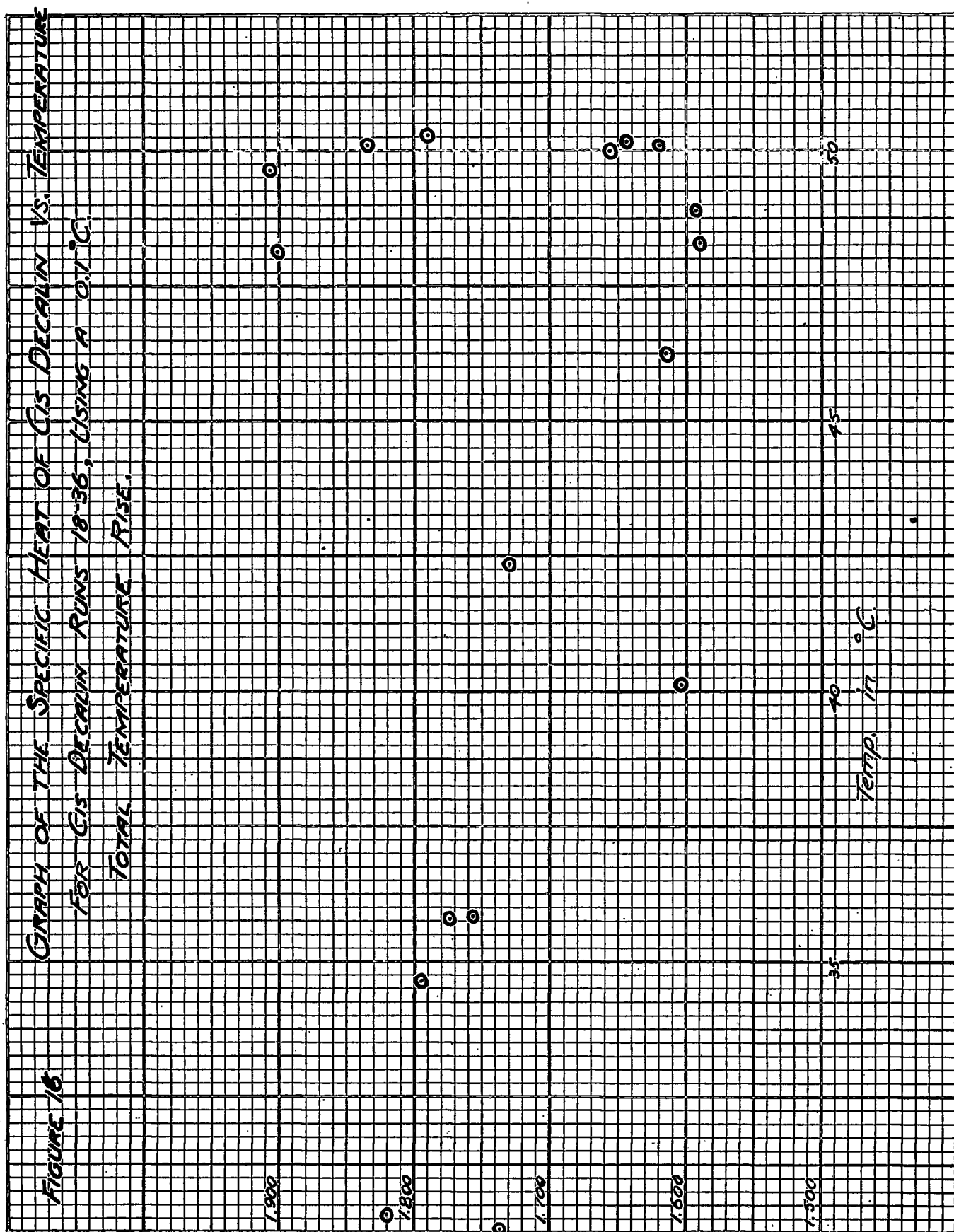
Run. No.	Avg. Decalin Temperature in °C	Total Temp of Decalin in °C	Specific Heat of Decalin in Joules /gm/°C
30	46.156	0.2350	1.6164
31	49.914	0.1352	1.6559
32	50.000	0.1388	1.6200
33	30.368	0.2253	1.8201
34	35.778	0.1543	1.7750
35	42.346	0.1510	1.7324
36	47.927	0.1649	1.5899

The results of table 16 are plotted on specific heat temperature axes but the points are so divergent that a curve through them would be meaningless.

#### 10. CONCLUSIONS

Figure 14 shows that, in runs 1-18 using about 1.5° C total temperature rise, the specific heat follows a fairly well defined curve. The values of the specific heat of cis decalin, however, are considerably higher than those found by either Mead or McLellan.

Figure 15 shows that in runs 19-36 using about 0.1° C total temperature rise the results are not reproducible. Hence an accurate graph in the range of the anomaly of 50.0-50.5°C is not feasible by the method as outlined in this thesis. It should be noted, however, that the readings taken from 50-50.5° do not indicate any abnormally large change in the specific heat



and thus do not, even qualitatively, give any evidence of an anomalous specific heat.

It can be concluded that the isothermal method is satisfactory for finding the specific heat of a liquid if a large total temperature rise is used, that is, something over one degree centigrade in the present apparatus.

#### 11. RECOMMENDATIONS FOR FURTHER WORK

A liquid whose specific heat is well defined from 0-150° C should be used in the present apparatus to see if the specific heat can be checked. This method would definitely show the limit of accuracy of the present apparatus.

The temperature measurements and control should be improved. A platinum resistance thermometer without quartz covering over the filament should be used to measure the bath temperature. This thermometer would eliminate temperature lags from the bath to resistance thermometer. The thermopile should have both junctions exposed to the respective liquids to again avoid temperature lags.

A great improvement in the present apparatus would result if the thermopile between the cup and the bath was eliminated. A platinum resistance thermometer without quartz covering should be inserted in the cup. This arrangement could be used to measure the temperature of the cup liquid and also to add the heating power to the liquid. This platinum resistance thermometer would eliminate the temperature lags experienced by the present thermopile. It would also simplify the apparatus in the calorimeter cup as the nicrome heating coil could be eliminated.

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