"The Determination of ~~the~~ Physical Properties

of the Cis and Trans Isomers

of Decahydronaphthalene."

by

Charles H. Davenport

A Thesis

Submitted in Partial Fulfillment

of the Degree of

Master of Applied Science in Chemical Engineering

The University of British Columbia

1938 - 1939.

Table of Contents.

Part 1

Part 11

Part lll

Part lV

Part V

Table of Diagrams.

Part 1.

During the last few years considerable research has been done on the hydrocarbon, decahydronaphthalene, ($C_{10}H_{18}$--abbreviated decalin), as it has been established that this compound exists in at least two isomeric forms; the cis and the trans. The great drawback to all investigation in this field regarding the isomeric structure lies in the fact that the two forms are very difficult to separate from one another in the pure state. The separation appears to be all the more complicated when we consider that there is always a possibility of partial conversion of one form to the other, and also that there is a possibility of there being more than two isomers present. Since the ultimate aim of the following research is to determine the variation with temperature of three of the physical properties of the cis and trans, a brief summary of previous investigation in this field will now be presented.

The first prediction of the existence of isomers of decalin was that of Mohr[1], who postulated the possibility of two stable forms. The existence of these, the cis and trans, has now been definitely established, but no agreement has yet been reached by different investigators as to the physical and chemical properties of each. A short time later, Wightman[2] showed that five isomers were possible for decalin.

In 1924, research on the subject was advanced by Willstatter and Seitz[3] who reported that they had prepared the cis form in

. . . .

1. Mohr, J. phy. Chem., 98, 315, (1918)   103, 316, (1922).
2. Wightman, J. Chem. Soc.,127, 1421 (1925).
3. Willstatter and Seitz, Berichte, 57B., 683-4 (1924).

six different ways at temperatures ranging from 20-80°C. Their product in all cases did not show variations greater than a few units in the 4th decimal place for either the densities or refractive indices. In the same year, N. O. Zelinsky[1] announced that he had isolated a 3rd isomer; that is, one distinct from either cis or trans. Further research by Zelinsky and M. B. Turova-Pollok[1] in 1925, showed that at 100°C. in the presence of a catalyst of aluminum bromide, cis could be transformed into the trans form. Also they claimed that other isomers of decalin were formed during the transformation process.

As previously stated, different investigators do not agree as to the physical and chemical properties of the isomers. For density, index of refraction and freezing point, W. Huckel[2] presents the following values:

| Trans decalin | d_4^{20} = .8695 | N_D^{20} = 1.46958 | F.P. = -36°C |
| Cis decalin | d_4^{20} = .8940 | N_D^{20} = 1.47950 | F.P. = -51°C |

According to Huckel, Herz[3] appears to have been the first to attempt the separation of the isomers by fractional distillation. Although Herz was unsuccessful, his methods suggested possibilities which were later realized in the research work carried on at the University of British Columbia.

At this University, the first work on this compound was carried on by L. M. Kirk[4], who, using decalin prepared by

. . . .

1. Zelinsky, N. O. and Turova-Pollak, M. B., Berichte, 58B., 1292-98 (1925).
2. Huckel, W., Annalen der Chemie; 441, 1 (1925)
3. Herz, Z. Physics. Chem. 101, 269 (1922).
4. Kirk, L. M., B. A. Sc., Thesis (1935)

D. Manley[1] by reduction of tetralin, obtained a partial separation of the cis and trans isomers. The method used was rectification at 100 mms. pressure, but it was later thought that if the rectification were at 10 mms. pressure, a better separation would be obtained since the difference in boiling point of the two isomers would be much increased. Also it was realized that at the higher pressures, the higher temperatures set up in the column, are apt to bring about decomposition or possibly rearrangement inside the decalin molecule.

Kirk's work was supplemented in the same year by that of W. F. Cornett[2] who carried out tests in various mixtures of the cis and trans isomers at temperatures of 20°C and 100°C, without the presence of a catalyst. This work indicated without doubt that cis was changed into trans, the rate of change being much greater at 100°C than at 20°C. However, no conclusive evidence was obtained for the reverse action, the changing of trans into cis.

The idea concerning the effect of lower pressure was now experimented with by R. D. Walker[3] in conjunction with Prof. W. F. Seyer[4]. Their method consisted in rectification at 10 mms. pressure, of technical decalin. In all, ten rectifications were made. Selected fractions of high percentage cis and trans were then recrystallized until no further change in freezing point

. . . .

1. Manley, D., B.A. Sc., Thesis (1934)
2. Cornett, W. F., B. A. Sc., Thesis (1935)
3. Walker, R. D., M. A. Sc., Thesis (1937)
4. Seyer, W. F., Assoc. Prof. in Chem. Eng., University of B. C.

could be detected, the result of this being about 150 c.c. of each isomer in what was thought to be a fairly high state of purity. The values they obtained for the physical constants are tabulated thus:

	Cis Decalin	Trans Decalin
Freezing Point ($^{\circ}$C)	-43.19 ± 0.2	-31.29 ± 0.2
Density (D_{20}^{4})	.8963	.8699
Index of Refraction (N_{20}^{D})	1.48113	1.46968

Determinations of freezing points were made for various mixtures of the two isomers, the results indicating that the eutectic temperature lies between -60° and -70°C. Also for these same mixtures, measurements were made of density and refractive index.

The above has been a presentation of the main available data on these isomers up to the present time. The following will show how we obtained substantial amounts of each pure isomer by following the Walker-Seyer method, and finally my determination of density, viscosity and surface tension over a temperature range.

1. Purification of the Technical Decalin Used.

The sample of decalin received from the Eastman Kodak Laboratories was yellow-orange in color, and contained various impurities of an aromatic nature. To remove these objectionable components, such a method as the following was used.

About 2 litres of sample were measured out and shaken
thoroughly in the cold with 400 c.c. of concentrated sulphuric
acid. After allowing the layers to separate, the black acid layer
was drawn off and discarded; the upper layer was collected and
subjected to a second similar treatment. A total of three such
acid treatments was required before the sample appeared practically
colorless.

To remove acid from the sample, it was now shaken with 100 c.c.
of 10% sodium carbonate solution, a persistent milkiness remaining
in both layers, even after standing overnight. The layers were
separated, and the upper layer was now shaken with 200 c.c. of 3%
sodium hydroxide solution. This again produced milkiness, but
gave well-defined layers. After separating again, the bottom
layer was tested with 2 drops of phenolphthalein, the resulting
pink color showing that all acid had been destroyed.

Now in order to render the sample neutral, it was washed
seven times with 200 c.c. portions of water. Slight milkiness
still persisted after this treatment.

The final step was to remove all traces of water and milkiness.
This was accomplished by first, filtering through a single sheet
of heavy filter paper to remove the bulk of the water, and second,
by filtering through a double sheet containing anhydrous calcium
chloride. Our sample of decalin now appeared as a colorless liquid.

2. The Rectification Apparatus.

The apparatus used for the rectifications was essentially
the same as that employed by R. D. Walker and Prof. W. F. Seyer.

The chief improvements consisted in the following:

(a) the use of electric heaters in place of gas burners for heating the column. This reduced the danger of heating surges, with the result that we could be fairly safe in interpreting temperature changes at the top of the column as being due to changes in the composition of the liquid distilling over. Hence improved separation of fractions could be expected.

(b) the mercury manometer was reconstructed in such a manner that an absolute vacuum could be maintained at all times above the mercury in the closed tube.

(c) when in operation, the apparatus was run continuously day and night until the completion of the rectification of the decalin charge.

The following description, along with the diagram, gives the details of the apparatus used.

(a) The Rectifying Column--This consisted of a glass tube, 1 inch in diameter and 95 inches long, with a 3000 c.c. glass bulb blown on its lower end. A small inlet tube was attached to the bulb. Except for the heating surface at the bottom and for a small peep hole in the side of the bulb, both column and bulb were completely lagged with asbestos. Also, in order to compensate for heat losses to the atmosphere, two heating coils of nichrome wire were wound in parallel about the column next to the glass, one coil covering the top, and the other the bottom half of the column. The accompanying graph, reproduced from the results of R. D. Walker and Prof. W. F. Seyer, shows the volts required across

Graph Showing Volts across Heating Coils
for Adiabatic Operation of the
Rectifying Column

Temperature Difference between Room & Top of Interior of Column (°C)

Volts across Heating Coils
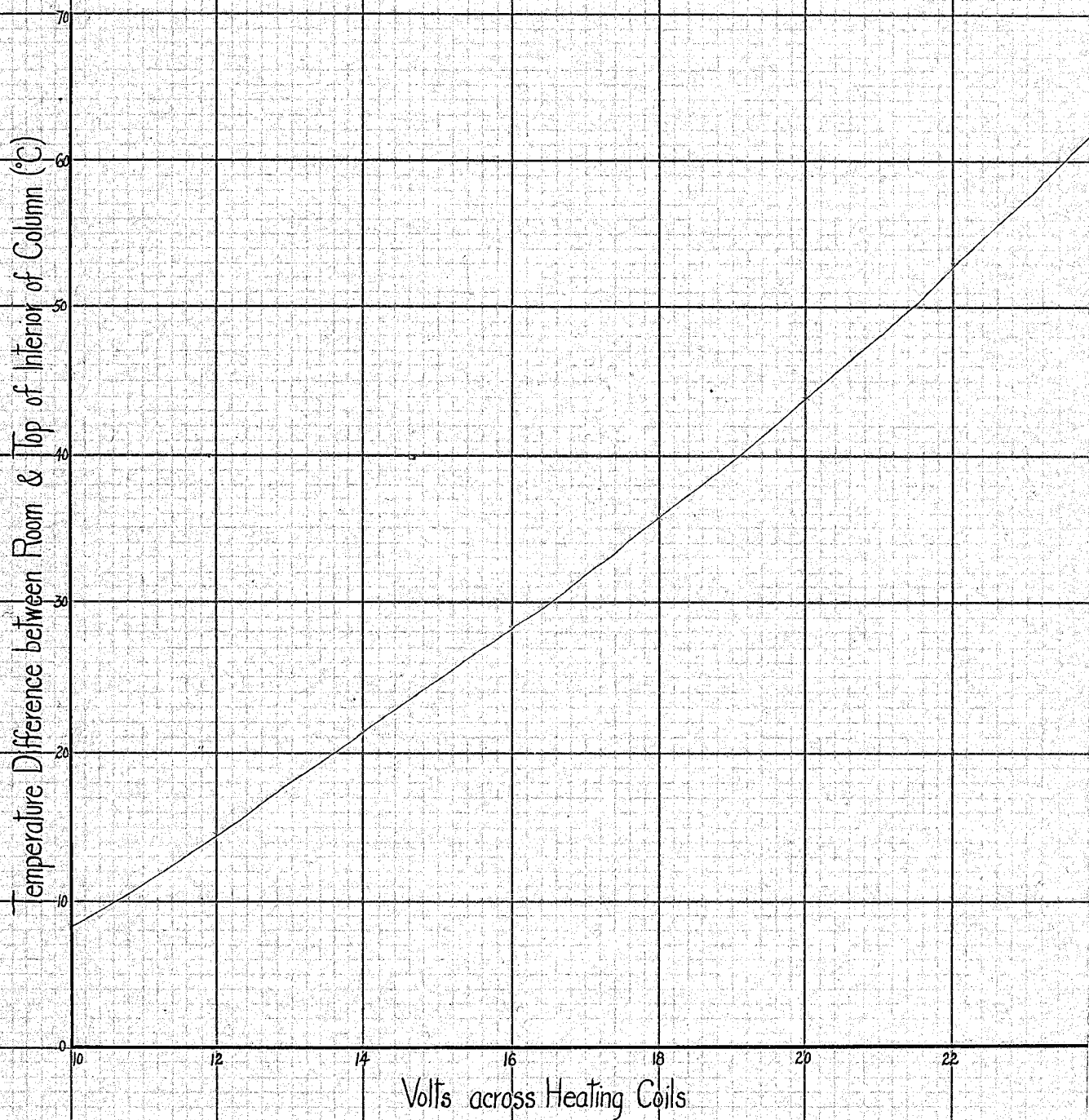
the double coil in order to maintain adiabatic operation. The interior of the column was packed with No. 18 galvanized-iron jack chain.

(b) The Condensing Unit--Blown on to the side of the column a few inches from the top, was the condensing unit. This was made up of two reflux condensers joined in parallel, and leading from the foot of this combination was a capillary tube through which the product was taken off. Also, a thermometer was inserted into the top of the column, extending down as far as the outlet tube to the condensers.

(c) The Receiving Unit--This apparatus, as the diagram shows, was made up of five receiving bulbs, all joined separately to the bottom of a glass casing. Running through the centre of this casing and fused on to it at the top, was the product tube from the condensers, the lower end of the tube possessing a small discharge spout. The spout could be rotated from one receiving bulb to the next by moving an electromagnet outside the glass casing, the result being that the magnet attracted small iron bars attached to the discharge tube, the whole then moving circularly on a pivot. To make sure that during distillation the discharge spout would not wander out of position when once set for a particular bulb, a permanent magnet was strapped to the side of the casing.

(d) The Pressure Manometers--A mercury manometer for measuring absolute pressure in the apparatus, and a differential sulphuric acid manometer for detecting small fluctuations in

APPARATUS FOR VACUUM, FRACTIONAL DISTILLATION OF DECALIN

VAPOUR TEMPERATURE THERMOMETER

CONDENSER WATER, THROUGH PUMP AND CONSTANT TEMPERATURE BATH

DOUBLE CONDENSER UNIT

DELIVERY TUBE WITH CAPILLARY CONSTRICTION

RECEIVING UNIT

IRON BARS

TUBE TO CENCO VACUUM PUMP

INLET TUBE FOR DRY ATMOSPHERIC AIR

DISCHARGE TUBE

RECEIVING BULBS

1 2 3 4 5

MERCURY MANOMETER

4 PRESSURE EQUALIZER BOTTLES

SULPHURIC ACID MANOMETER

COLUMN, ASBESTOS-LAGGED, AND SURROUNDED BY HEATING COILS OF NICHROME WIRE

INLET TUBE TO BULB

ELECTRIC HEATER

pressure, were employed. The latter was 7.3 times as sensitive as the former. The mercury manometer was only used at the beginning of a run until pressure equilibrium was established; then the stopcock on one link of the acid manometer was closed, and future pressure changes were observed on this scale.

3. The Separation of Cis and Trans Decalin.

(a) The Experimental Procedure--As previously stated, each rectification was made continuous; that is, for each batch of decalin used in the column bulb, the rectification was carried on day and night until all but a little liquid residue remained in the bulb. Readings were made every hour of vapour temperature, room temperature, condenser water temperature, and also of pressure. In this way we were able to maintain adiabatic operation of the column, and obtain good separation of the various fractions. Moreover, it enabled us to keep good check on the pressure (which was kept as close as possible to 10 mms. of mercury), but little difficulty was experienced here, for once the levels had come to equilibrium, they usually would remain constant for hours at a time. Slight variations in pressure were corrected for by adjusting a stopcock which connected the apparatus through a drying tube to the atmosphere. The four Winchester bottles as shown in the diagram and having a total capacity of 10 litres, served as pressure equalizers.

It may here be mentioned that the reflux ratio in the apparatus could not be measured but could only be judged by observation of the amount of vapour condensing. It was found

that the number of drops per minute overflow through the
capillary and discharge tubes had a tendency to decrease
slightly as the rectification proceeded. However, the reflux
ratio was kept as constant as possible by controlling the
temperatures and the amounts of condenser water used. The
condenser water was pumped from a large constant-temperature
bath.

(b) The Experimental Results--In the following tabulations
will be found the results of our four rectifications. The
first two, it will be noted, were run using our washed decalin,
the purpose being to obtain sufficient quantities of the
particular fractions which were high in cis or trans content.
Then, using these high percentage fractions, we combined them
in the third and fourth rectifications respectively, in order
to obtain our final high cis and trans fractions.

The refractive index at 20°C. and for D-sodium light was
recorded for each fraction, use being made of a Pulfrich
refractometer. Then, employing the refractive indices of pure
cis and trans as determined by R. D. Walker and W. F. Seyer
and assuming a linear relationship between the indices and
composition, the accompanying graph was constructed. From this
graph, the approximate composition of each fraction could be
read off.

Other data and general information concerning the rectifications,
appears in the following results.

Graph Showing Variation of Index of
Refraction with Composition

Index of Refraction

1·4850
1·4825
1·4800
1·4775
1·4750
1·4725
1·4700

0   25   50   75   100

% of Cis Isomer
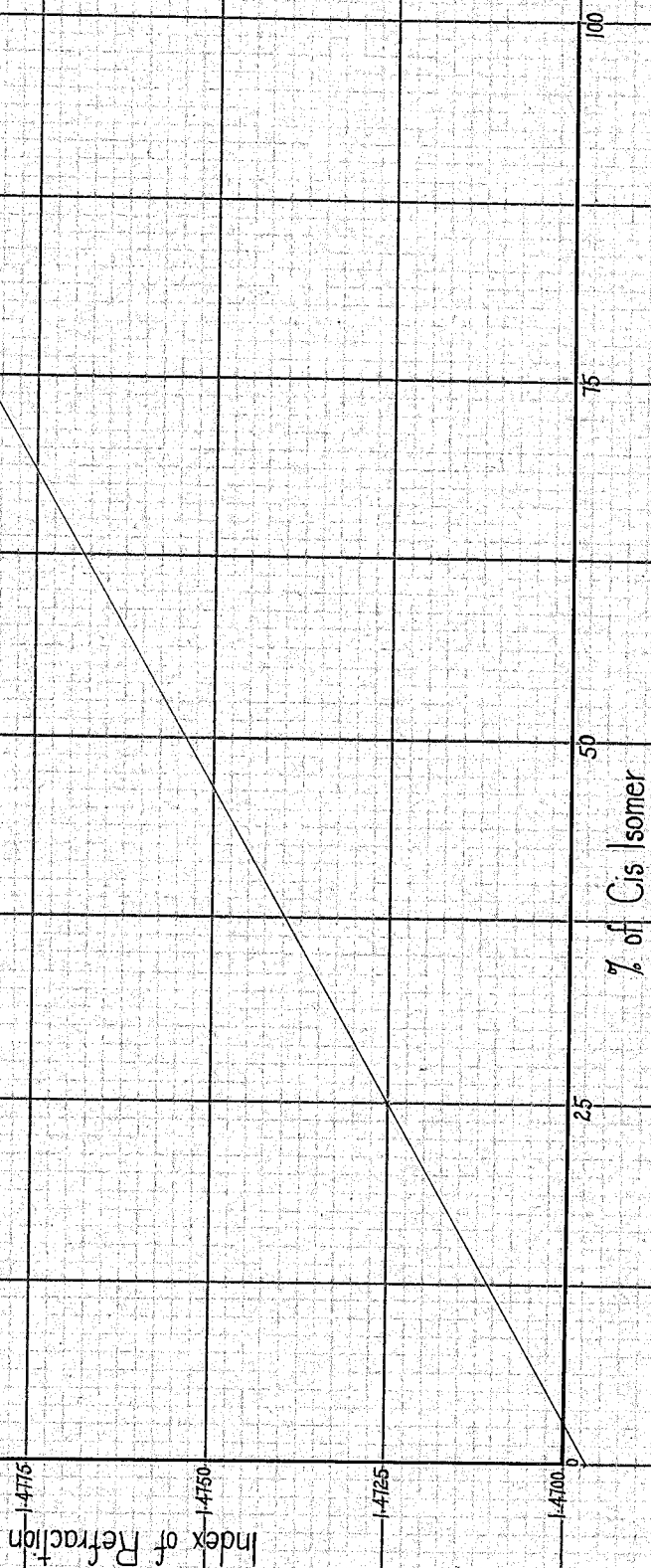
Rectification No. 1   October 16--October 20, 1937.

Characteristics of Charge:

(a) 2000 c.c. of washed decalin (Eastman Kodak)

(b) D_{20}^{4} = .8920

(c) N_{20}^{D} = 1.47965

(d) approximate composition - 87% cis

	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
Boiling Point of Fraction ($^{\circ}$C)	60.8-64.0	63.9-64.2	64.2-67.8	67.8-69.2	69.2-63.0
Volume of Fraction (c.c.)	121	332	743	352	290
Time for Fraction (hrs.)	3.75	12.0	34.0	20.5	15.5
Rate of Fractionation (c.c./hr.)	32.3	27.7	21.9	17.2	18.7
Index of Refraction (N_{20}^{D})	1.47081	1.47170	1.47975	1.48113	1.48229
Approximate Composition (% of cis)	9	18	88	99	>100

Final residue in column bulb = 40 c.c.

Hence total loss during rectification = 122 c.c.

The fact that the first fractions (that is, those with the lower boiling points) were high in trans content, indicated that of the two isomers, trans has the lower boiling point. The analysis of Bulb 5 shows the presence of impurities of high boiling point, they being such that their indices of refraction had considerable influence on the index of pure cis. Evidently, these impurities were not affected by the initial washing treatment.

Rectification No. 2

Characteristics of Charge:

(a) 2025 c.c. of washed decalin (Eastman Kodak)

(b) D_{20}^{4} = .8920

(c) N_{20}^{D} = 1.47965

(d) approximate composition = 87% cis

	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
Boiling Point of Fraction (^{o}C)	57.0-62.4	62.4-64.4	64.4-67.4	67.4-73.2	------
Volume of Fraction (c.c.)	225	240	745	403	------
Time for Fraction (hrs.)	10.5	14.5	56.0	30.0	------
Rate of Fractionation (c.c./hr.)	21.4	16.6	13.3	13.4	------
Index of Refraction (N_{20}^{D})	1.47076	1.47455	1.48098	1.48283	------
Approximate Composition (% of Cis)	8	43	97	>100	------

Final residue in column bulb = 97 c.c.

Hence total loss during rectification = 315 c.c.

Although the same type of decalin was used for this rectification as was used for the first, it was found this time that four main fractions, instead of five, could be obtained. This was probably due to better control and separation during this rectification, since we used a smaller rate of product discharge. The high boiling point impurities again appear in our last fraction.

Rectification No. 3   October 30--November 4, 1937.

Characteristics of Charge:

(a) 1725 c.c. of high cis decalin, comprising bulbs 4 and

5 of Rectification No. 1 and bulbs 3 and 4 of Rectifi-

cation No. 2.

(b) N_{20}^D = 1.48166

(c) approximate composition = >100% cis

	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
Boiling Point of Fraction (^oC)	60.4-63.5	63.5-66.7	64.5-67.8	67.8-66.9	66.9-64.6
Volume of Fraction (c.c.)	162	423	540	203	114
Time for Fraction (hrs.)	18.0	42.0	38.5	13.5	13.0
Rate of Fractionation (c.c./hr.)	9.0	10.0	14.0	15.0	8.8
Index of Refraction (N_{20}^D)	1.48024	1.48108	1.48113	1.48118	1.48118
Approximate Composition (% of cis)	92.5	100	100	100	100

Final residue in column bulb = 95 c.c.

Hence total loss during rectification = 188 c.c.

Bulbs 3, 4 and 5 were obtained with the rectification pressure slightly less than that used for bulbs 1 and 2. Our high cis decalin was now concentrated in the last four bulbs, the chief impurities being in the bulb 1.

Before proceeding with the trans, the column was now washed thoroughly by refluxing in it for 7 hours a charge of decalin which had an approximate composition of 37% trans. This washing charge was made up of three fractions obtained from the R. D. Walker - W. F. Seyer rectifications.

Rectification No. 4   November 16 -- November 19, 1937.

Characteristics of Charge:

(a) 1490 c.c. of high trans decalin, comprising bulbs 1 and 2 of Rectification No. 1; bulb 1 of Rectification No. 2; and 3 washed high trans fractions from the R. D. Walker-W. F. Seyer rectifications.

(b) N_{20}^D = 1.46987

(c) approximate composition = 100% trans.

	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
Boiling Point of Fraction ($^\circ$C)	50.5-64.0	64.0-60.2	60.2-59.5	59.5-60.9	60.9-61.8
Volume of Fraction (c.c.)	230	490	240	195	141
Time for Fraction (hrs.)	8.0	23.5	13.5	11.5	8.5
Rate of Fractionation (c.c./hr.)	28.7	20.9	17.8	17.0	16.6
Index of Refraction (N_{20}^D)	1.46192	1.46918	1.46958	1.46968	1.47100
Approximate Composition (% trans)	>100	>100	100	100	89

Final residue in column bulb = 165 c.c.

Hence total loss during rectification = 29 c.c.

From the index graph, it appears that the index for the fraction in bulb 1 is very much smaller than the accepted index for pure trans. Thus bulb 1 must have contained a great deal of some low-boiling inpurity.

4. The Final Purification of Cis and Trans Decalin by Fractional Crystallization.

This method of purification is based on the formation of a eutectic when a mixture of cis and trans decalin is frozen. Thus, if we have decalin containing a certain percentage of trans, and we cool it slowly, there will be a certain temperature at which trans crystals commence to separate out. This separation of trans crystals will continue with further cooling until we reach the eutectic temperature, at which point all remaining liquid will freeze to give the eutectic mixture. Since the eutectic mixture will be of no use to us, then, in order to obtain the high trans by this method, it will be necessary to stop cooling before reaching the eutectic temperature and to pour off the remaining liquid. The trans crystals obtained, along with a little of the clinging liquid, will consequently be of higher trans content than the original decalin mixture. If we repeat the process now with the crystal mixture obtained, we will remove a little more liquid, and finally, after doing many of these crystallizations, will arrive at the stage where the removal of a portion of liquid will not lower the temperature at which crystals first separate out. This condition will then indicate that the liquid is pure, and the constant temperature will be the true freezing point.

(a) The Apparatus and Experimental Procedure--The accompanying diagram shows the set-up of apparatus employed, and very little additional explanation is required. It may be mentioned that a vertical line-image was formed on the graduated glass scale, and when the bridge was balanced, this line was at the centre of the
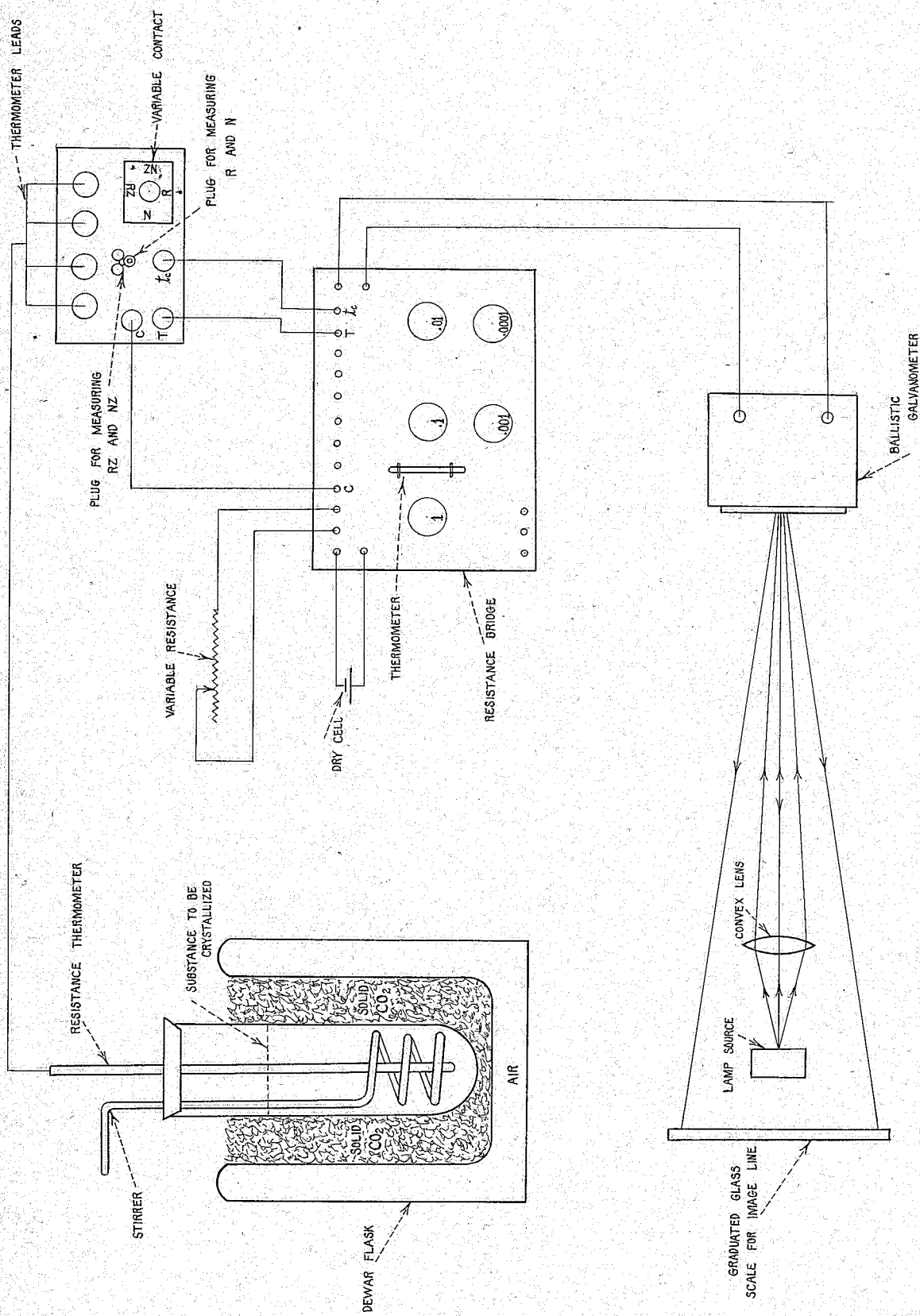
APPARATUS FOR PURIFICATION
BY RECRYSTALLIZATION
OF THE ISOMERS OF DECALIN

scale. Resistance readings could be converted to temperatures by application of Callendar's formulae.

The liquid to be purified was placed in a large glass tube in the Dewar, and was cooled by the surrounding medium of solid carbon dioxide. During the first few crystallizations, mechanical stirring was employed, but this had the disadvantage of leaving a thick crust of crystals around the periphery of the Dewar, with the result that the heat transfer was lowered and the thermometer could not be kept surrounded with liquid at all times. Hence, toward the end of purifications, hand stirring was employed for each run.

In carrying through a crystallization, the liquid was cooled slowly until a constancy was obtained in the resistance readings. This corresponded to cis (or trans, as the case may be) crystallizing out, and the times of constancy could be used for judging relative purities of successive crystallizations. When pure, there was no eutectic, and the temperature was constant for the greatest time. When the temperature started to drop again, it was in each case observed for several minutes, and then the remaining liquid was decanted off.

Supercooling was one of the chief difficulties experienced. We found that this could be minimized usually by vigorous hand stirring and by using a slow rate of heat transfer; when these methods failed, seeding was always successful.

(b) Experimental Results for Cis Decalin--The fractions selected for the purification were bulbs 2,3,4 and 5 of Rectification No. 3. It required about twenty separate crystallizations to obtain

the pure isomer, the final volumetric yield being 313 c.c.
An appreciable amount of water was absorbed from the atmosphere
during the purification, but this was easily removed by treat-
ment with metallic sodium, and then by filtration. In order
to give a low rate of heat transfer in the final stages, the
liquid was placed in a large glass tube possessing a hollow
wall (resembling a Dewar), the hollow space containing air.
Also, at the same time, the dry ice medium was replaced by one
of methyl alcohol containing dry ice. The temperature of this
medium was maintained at -55°C., and was measured with a pentane
thermometer.

For cis decalin our final result is:

F.P. = -43.26 $\pm$ .04 °C. and N_{20}^D = 1.48113

R. D. Walker and W. F. Seyer gave:

F.P. = -43.19 $\pm$ .2 °C. and N_{20}^D = 1.48113

(c) Experimental Results for Trans Decalin--The purification
of this isomer gave considerable trouble. From a large number
of crystallizations based, first, on bulb 2, and second, on
bulbs 3 and 4, all of Rectification No. 4, it was discovered
that no constancy in freezing point could be obtained. This
fact appeared to indicate the presence of some impurity whose
index of refraction, freezing point and boiling point, are very
close to that of trans decalin. The presence of such a substance

appears all the more remarkable when we consider that it did not give trouble at this stage in the research of R. D. Walker and W. F. Seyer. Since these investigators used unwashed decalin in their rectifications, it seems possible that the presence of other impurities (that are removed by washing) must in some way help to cause the removal of this impurity encountered in our high trans fractions.

To avoid further loss of time, we considered it advisable to fractionate a quantity of unwashed decalin. The results obtained are now presented.

5. Results of the 2nd Series of Rectifications and
Crystallizations of Trans Decalin.

Rectification No. 1 (a)　　　　January 6--January 8, 1938.

Characteristics of Charge:

(a) 2000 c.c. of unwashed decalin (Eastman Kodak)

(b) D_{20}^{4} = .8890

(c) N_{20}^{D} = 1.47829

(d) approximate composition = 23% trans.

	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
Boiling Point of Fraction (^{O}C)	70.7-72.2	72.2-69.0	69.0-68.0	68.0-69.9	69.9-73.1
Volume of Fraction (c.c.)	288	135	140	173	92
Time for Fraction (hrs.)	17.0	9.0	8.0	12.0	8.0
Rate of Fractionation (c.c./hr.)	16.9	15.0	17.5	14.4	11.5
Index of Refraction (N_{20}^{D})	1.46938	1.46958	1.46983	1.47150	1.47760
Approximate Composition (% trans)	>100	100	100	84	31

The pressure was slightly greater in this rectification than in previous ones. It will be noted from the compositions obtained that very good rectification was accomplished. This was due to our maintenance of a slow rate of discharge, and also to the fact that we distilled over less than half of the bulb charge, since we were not concerned now with the cis isomer (which has the higher boiling point). The fractions obtained were spread over the 5 bulbs to give better separation.

Rectification No. 2 (a)

Characteristics of Charge:

(a) 1380 c.c. of Eastman Kodak decalin (unwashed) as used in Rectification No. 1(a) plus bulbs 2, 3 and 4 of Rectification No. 4.

	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
Boiling Point of Fraction ($^{\circ}$C)	59.8-62.0	62.0-62.4	62.4-61.6	61.6-61.5	-----
Volume of Fraction (c.c.)	325	180	361	380	-----
Time for Fraction (hrs.)	18.5	10.0	19.0	27.0	-----
Rate of Fractionation (c.c./hr.)	17.6	18.0	19.0	14.1	-----
Index of Refraction (N_D^{20})	1.46898	1.46968	1.46968	1.46987	-----
Approximate Composition (% trans)	>100	100	100	99.5	-----

The high quality of fractions 2 and 3 as indicated by index measurements suggested the possibility of further purification by recrystallization. This was attempted, but it was found that a constant freezing point could not be obtained. A third rectification was therefore necessary.

Rectification No. 3 (a)   January 26--January 28, 1938.

Characteristics of Charge:

(a) 820 c.c., comprising bulbs 2,3 and 4 of
Rectification No. 2(a).

	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
Boiling Point of Fraction ($^{\circ}$C)	65.8-66.9	66.9-67.3	67.3-69.2	69.2-69.3	69.3-68.1
Volume of Fraction (c.c.)	76	252	167	238	76
Time for Fraction (hrs.)	4.5	14.0	9.0	13.0	6.0
Rate of Fractionation (c.c./hr.)	17.0	18.0	18.5	18.3	12.6
Index of Refraction (N_{20}^D)	1.46908	1.46953	1.46958	1.46953	1.46953
Approximate Composition (% trans)	>100	100	100	100	100

The above represents our final rectification. The pressure was maintained higher than previously, being kept at about 18 mms.

Bulbs 2,3,4 and 5 were now combined together and subjected to the crystallization treatment. It was found that about eight crystallizations were required in order to obtain the constant freezing point, and that the volumetric yield of the pure isomer was 165 c.c. Evidently, the effect of the higher pressure was a beneficial factor in the removal of the conflicting impurities.

For trans decalin, our final result is:

F. P. = $-31.49 \pm .2$ $^{\circ}$C. and N_{20}^D = 1.46953

R. D. Walker and W. E. Seyer gave:

F. P. = $-31.29 \pm .2$ $^{\circ}$C. and N_{20}^D = 1.46968

PART II

The Determination of Physical Constants of Cis and Trans Decalin

Section 1--Variation with Temperature of Density

The method employed for this purpose was an application of Archimedes' Principle (see accompanying diagram). The formulae employed may be derived as follows:

Let: T = true mass of plummet in vacuum

Wair = mass of plummet in dry air   )

Wwa = mass of plummet in pure water) - at temperature of $t^{\circ}C$.

Wli = mass of plummet in decalin

Pair = density of dry air

Pwa = density of pure water

Pli = density of decalin

V = volume of plummet at $t^{\circ}C$.

Assume a neglible buoyant effect of liquids on immersed portion of wire

∴ T - Wair = V Pair

and T - Wwa = V Pwa

$$\therefore V = \frac{Wair - Wwa}{Pwa - Pair}$$

To obtain Pli we again use this formula, substituting Pair by Pli

$$\therefore Pli = Pwa + \frac{Wwa - Wli}{V}$$

The standard value of t employed in my determinations was $20.00^{\circ}C.$, and the values of Wwa_{20} and $P^4_{wa_{20}}$ were used as equation constants. Hence:

$$P^4_{li} = P^4_{wa_{20}} + \frac{Wwa_{20} - Wli\,t^{\circ}}{V\,t^{\circ}}$$

APPARATUS FOR DETERMINATION OF DENSITY, SURFACE TENSION & VISCOSITY OF ISOMERS OF DECALIN

BALANCE

OVERHEAD PLATFORM

SUSPENSION FOR DENSITY DETERMINATIONS

MOTOR-DRIVEN STIRRER

RESISTANCE THERMOMETER CONNECTED TO RESISTANCE BRIDGE

LEADS TO THERMOSTATIC CONTROL

OSTWALD VISCOMETER

SPADE HEATER

WIRE HEATER FOR CLOSE TEMPERATURE CONTROL

SURFACE TENSION APPARATUS

SENSITIVE LIQUID TUBE FOR AUTOMATIC THERMOSTAT

DECALIN SAMPLES

GLASS CONTAINER, LAGGED, AND EXTERNALLY LINED WITH HEATING COIL

BATH LIQUID (OIL, WATER OR ALCOHOL)

Having got V_{20} from air-water measurements, Vt^o could be calculated from

$$Vt^o = V_{20} + (V_{20})(t-20.00)(.000038)$$

where   .000038 = coefficient of cubical expansion of ⎫
                     quartz glass plummet   ⎬ from
$$P^4_{wa_{20}} = .99823$$ ⎬ International
$$P^4_{air_{20}} = .00120$$ ⎭ Critical Tables

(a) Observations and Calculations for Cis Decalin

Mass of suspension (constant)	= .1219 gr.
Mass of suspension + plummet in pure water at 20.00°C.	= 22.6381 gr.
∴ Mass of plummet in pure water at 20.00°C.	= 22.5162 gr.
Mass of plummet in dry air at 20.00°C.	= 31.0059 gr.
∴ Volume of plummet at 20.00°C. (from formula)	= 8.5150 c.c.

Temperature ($T^oC.$)	Mass of suspension + Plummet (gr)	Mass of plummet (gr)	Volume of plummet (V_t c.c.)	Density (D_t^4) of decalin
-40.00				
-30.00	23.1751	23.0532	8.4988	.9350
-20.00	23.2402	23.1183	8.5020	.9274
-10.00	23.3068	23.1849	8.5053	.9196
0.00	23.3715	23.2496	8.5085	.9120
10.00	23.4366	23.3147	8.5117	.9044
20.00	23.5020	23.3801	8.5150	.8967
30.00	23.5665	23.4446	8.5182	.8892
40.00	23.6311	23.5092	8.5215	.8817
50.00	23.6955	23.5736	8.5247	.8742
60.00	23.7599	23.6380	8.5279	.8667
70.00	23.8243	23.7024	8.5312	.8592
80.00	23.8873	23.7654	8.5344	.8519
90.00	23.9527	23.8308	8.5376	.8442
100.00	24.0169	23.8950	8.5409	.8368
110.00	24.0804	23.9585	8.5441	.8294
120.00	24.1460	24.0241	8.5473	.8218
130.00	24.2101	24.0882	8.5506	.8144
140.00	24.2773	24.1554	8.5538	.8066
150.00	24.3467	24.2248	8.5570	.7986
160.00	24.4154	24.2935	8.5603	.7906
170.00	24.4857	24.3638	8.5635	.7825
180.00	24.5551	24.4332	8.5668	.7745

(b) Observations and Calculations for Trans Decalin.

Temperature ($T^oC.$)	Mass of suspension + Plummet (gr)	Mass of plummet (gr)	Volume of plummet (Vt c.c.)	Density (D_t^4) of decalin
-40.00				
-30.00	23.4114	23.2895	8.4988	.9072
-20.00	23.4757	23.3538	8.5020	.8997
-10.00	23.5396	23.4177	8.5053	.8922
0.00	23.6027	23.4808	8.5085	.8849
10.00	23.6658	23.5439	8.5117	.8775
20.00	23.7296	23.6077	8.5150	.8700
30.00	23.7927	23.6708	8.5182	.8627
40.00	23.8559	23.7340	8.5215	.8553
50.00	23.9190	23.7971	8.5247	.8480
60.00	23.9831	23.8612	8.5279	.8405
70.00	24.0472	23.9253	8.5312	.8331
80.00	24.1120	23.9901	8.5344	.8255
90.00	24.1781	24.0562	8.5376	.8178
100.00	24.2424	24.1205	8.5409	.8104
110.00	24.3106	24.1887	8.5441	.8025
120.00	24.3736	24.2517	8.5473	.7952
130.00	24.4390	24.3171	8.5506	.7876
140.00	24.5063	24.3844	8.5538	.7798
150.00	24.5764	24.4545	8.5570	.7717
160.00	24.6448	24.5229	8.5603	.7638
170.00	24.7164	24.5945	8.5635	.7555
180.00	24.7865	24.6646	8.5668	.7474

Section 11--Variation With Temperature of Viscosity

For viscosity measurements, an Ostwald viscometer was employed. This was suitably suspended, along with the surface tension and density-measuring apparatus, in a constant-temperature bath, thermostatically controlled. (see accompanying diagram).

The mathematical relation employed was the well known equation for relative viscosities

i.e. $$\frac{U_1}{U_2} = \frac{d_1 t_1}{d_2 t_2}$$

in which, for two liquids 1 and 2, "U", "d" and "t" are respectively absolute viscosity, density and time to flow through the capillary employed. Hence, by knowing the values of "U" and "d" at some stated temperature for a particular liquid, one may measure "t" at that temperature, and then, using these values, obtain a constant in the above equation. This constant will be satisfactory for other temperatures, however, only when we assume the absence of changes in the dimensions of the capillary. The standardizing liquid used in my experiments was pure benzene, and the standardizing temperature was $20^{\circ}C$.

(a) Observations and Calculations for Cis Decalin

Density of benzene at $20^{\circ}C$ = .8787 gr/c.c.)   from

Absolute viscosity of benzene at $20^{\circ}C$ = .00649   )- International Critical Tables

Observed time for benzene to run down capillary = 78.3 sec.

$\therefore$ Constant $\left(\frac{U_2}{d_2 t_2} \right. = \frac{.00649}{(78.3)(.8787)} = .00009433$

$\therefore$ Working Equation is: $U = (t)(d)(.00009433)$

Temperature $(T^\circ C)$	Density (D_T^4)	Time to flow through capillary (t sec.)	Absolute viscosity of decalin (U_T^4)
-40.00			
-30.00	.9350	1730.0	
-20.00	.9274	1240.0	.15259
-10.00	.9196	851.0	.10848
0.00	.9120	636.0	.07382
10.00	.9044	489.5	.05472
20.00	.8967	392.8	.04176
30.00	.8892	319.4	.03323
40.00	.8817	266.0	.02679
50.00	.8742	224.5	.02212
60.00	.8667	192.2	.01851
70.00	.8592	167.5	.01571
80.00	.8519	149.5	.01358
90.00	.8442	132.5	.01201
100.00	.8368	117.4	.01055
110.00	.8294	105.6	.00927
120.00	.8218	95.7	.00826
130.00	.8144	87.8	.00742
140.00	.8066	80.4	.00674
150.00	.7986	74.5	.00612
160.00	.7906	69.0	.00561
170.00	.7825	64.5	.00515
180.00	.7745	60.2	.00476
			.00440

(b) <u>Observations and Calculations for Trans Decalin.</u>

Temperature (T^oC)	Density (D_T^4)	Time to flow through capillary (t sec.)	Absolute viscosity of decalin (U_T^4)
-40.00			
-30.00	.9072	853.0	.07300
-20.00	.8997	629.8	.05345
-10.00	.8922	484.9	.04081
0.00	.8849	383.5	.03201
10.00	.8775	310.6	.02571
20.00	.8700	258.3	.02120
30.00	.8627	219.4	.01785
40.00	.8553	187.0	.01509
50.00	.8480	161.3	.01290
60.00	.8405	141.1	.01119
70.00	.8331	125.5	.00986
80.00	.8255	112.6	.00877
90.00	.8178	102.0	.00787
100.00	.8104	92.5	.00707
110.00	.8025	84.2	.00637
120.00	.7952	77.0	.00578
130.00	.7876	72.1	.00536
140.00	.7798	66.6	.00490
150.00	.7717	63.0	.00459
160.00	.7638	58.6	.00422
170.00	.7555	54.5	.00388
180.00	.7474	51.2	.00361

Section 111--Variation with Temperature of Surface Tension.

Determinations of surface tension were carried out employing the method of Richards, Speyers and Carver[1] (see accompanying diagram). Their equation is of the form

$$\gamma = KHd$$

where
γ = surface tension

d = density of liquid used

K = constant

H = difference in levels in the two tubes, corrected for the meniscuses.

The value of H is given by the equation

$$H = (h_1 - h_2) + \frac{(r_1 - r_2)}{3} - .1288 \left(\frac{r_1^2}{h_1^2} - \frac{r_2^2}{h_2^2} \right)$$

where h_1 and h_2 = observed heights of capillary in the two tubes above plane surface.

r_1 and r_2 = radii of the two tubes.

Since the last term is neglible in this work, the equation becomes

$$H = (h_1 - h_2) - \frac{(r_2 - r_1)}{3}$$

The constants K, r_1 and r_2 for the apparatus used in my measurements were determined by R. Bennett[2] by calibration with pure benzene. Their values are:

K = 23.63 dynes. cms./gr. (corrected for meniscuses)

r_1 = .033 cms.

r_2 = .121 cms.

. . . .

1. Richards, Speyers and Carver; J. Am. Chem. Soc., 46, 1196 (1924).
2. Bennett, R., B. A. Sc., Thesis (1935).

(a) Observations and Calculations for Cis Decalin

Temperature (T°C)	Difference in levels ($h_1 - h_2$ cms.)	Corrected Difference in levels (H cms.)	Density (D_t^4)	Surface Tension of Decalin (γ_T^4 dynes/cm)
-40.00				
-30.00	1.750	1.721	.9350	38.02
-20.00	1.710	1.681	.9274	36.83
-10.00	1.670	1.641	.9196	35.65
0.00	1.630	1.601	.9120	34.50
10.00	1.590	1.561	.9044	33.36
20.00	1.548	1.519	.8967	32.18
30.00	1.505	1.476	.8892	31.01
40.00	1.460	1.431	.8817	29.81
50.00	1.415	1.386	.8742	28.63
60.00	1.380	1.351	.8667	27.67
70.00	1.350	1.321	.8592	26.82
80.00	1.315	1.286	.8519	25.88
90.00	1.280	1.251	.8442	24.95
100.00	1.245	1.216	.8368	24.04
110.00	1.210	1.181	.8294	23.14
120.00	1.175	1.146	.8218	22.25
130.00	1.140	1.111	.8144	21.38
140.00	1.108	1.079	.8066	20.56
150.00	1.076	1.047	.7986	19.76
160.00	1.040	1.011	.7906	18.89
170.00	1.005	.976	.7825	18.04
180.00	.968	.939	.7745	17.18

(b) Observations and Calculations for Trans Decalin.

Temperature (T^oC)	Difference in levels ($h_1 - h_2$ cms.)	Corrected Difference in levels (H cms.)	Density (D_T^4)	Surface Tension of Decalin (γ_T^4 dynes/cm)
-40.00				
-30.00	1.675	1.646	.9072	35.29
-20.00	1.635	1.606	.8997	34.14
-10.00	1.592	1.563	.8922	32.95
0.00	1.555	1.526	.8849	31.91
10.00	1.518	1.489	.8775	30.87
20.00	1.483	1.454	.8700	29.89
30.00	1.445	1.416	.8627	28.87
40.00	1.405	1.376	.8553	27.81
50.00	1.365	1.336	.8480	26.77
60.00	1.329	1.300	.8405	25.82
70.00	1.290	1.261	.8331	24.82
80.00	1.257	1.228	.8255	23.95
90.00	1.220	1.191	.8178	23.02
100.00	1.179	1.150	.8104	22.02
110.00	1.139	1.110	.8025	21.05
120.00	1.105	1.076	.7952	20.22
130.00	1.071	1.042	.7876	19.39
140.00	1.041	1.012	.7798	18.65
150.00	1.008	.979	.7717	17.85
160.00	.970	.941	.7638	16.98
170.00	.935	.906	.7555	16.17
180.00	.903	.874	.7474	15.44

PART III

The Mathematical Treatment of the Experimental Results.

The following work represents an extensive study of the results obtained for the three physical properties of cis and trans decalin. For the most part it involves the application of well-known formulae, the main object being to secure values for various theoretical quantities and constants, and to note the effect of temperature on these values. By this means, several conclusions are drawn regarding transitions in the structure of decalin. Also, in this work, values for such quantities as latent heats of vaporization and fusion, critical temperature, etc. were calculated, the object being to have these calculated quantities as guides in further research to be done on the decalin.

1. A Study of the Plotted Results for the Physical Properties of Cis Decalin.

The accompanying graph shows the effect of temperature on the physical properties of cis decalin. Close examination of these curves shows that each is marked by characteristic breaks, indicating possible transitions. It will be noticed that the curve for surface tension is linear but shows a break at 50° - 60° and another at 120° - 130° C.; the curve for logarithm of viscosity is linear but shows four breaks at approximate temperatures of -5° - 0° C.; 35° - 40° C.; 60° - 70° C.; 120° - 130° C.

After the cooling down to -30° C., the physical properties were remeasured at 20° C. Since no changes were observed the following conclusions may be drawn:

Graph Showing Variation with Temperature
of Surface Tension, Density & Viscosity of
Cis Decalin

Surface Tension

Density

Logarithm of Viscosity

Temperature (°C)

-30 -10 0 10 30 50 70 90 110 130 150 170

Surface Tension

36.0
35.0
32.0
29.0
26.0
23.0
20.0
17.0
14.0

Density

.94
.92
.90
.88
.86
.84
.82
.80
.78

Logarithm of Viscosity

1.00
1.20
1.40
1.60
1.80
2.00
2.20
2.40
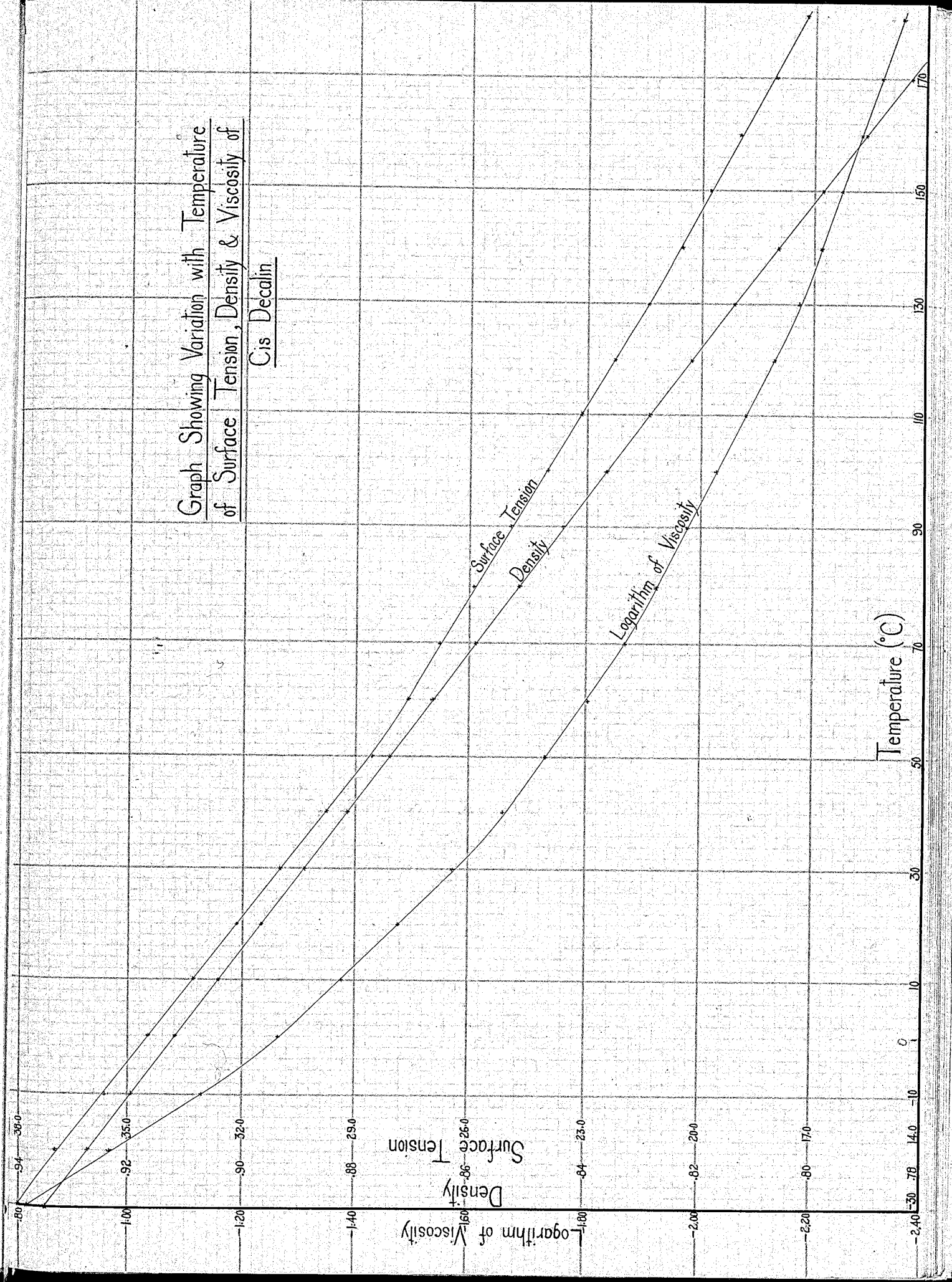
(1) if a transition from one form to another does take place on lowering the temperature, then the form produced must be very unstable at 20° C.

(2) if a transition to a form stable at 20° C does occur on lowering the temperature, then the transition must be a time reaction, requiring a much longer time than was used in these experiments.

Similarly, after the heating to 180° C., the physical properties were remeasured at 20° C. Considerable changes were discovered, as the following record shows:

(1) in surface tension apparatus, H had increased to 1.551 cms., corresponding to γ_{20} = 32.92. This is an increase of 2.30% over the true value γ_{20} = 32.18 for cis decalin.

(2) in density apparatus, the mass of suspension + plummet had decreased to 23.4902 gr., corresponding to D_{20}^4 = .8982. This is an increase of .17% over the true value D_{20}^4 = .8967 for cis decalin.

(3) in viscosity apparatus, the time had increased to 403.5 sec., corresponding to U_{20} = .03419. This is an increase of 2.89% over the true value U_{20} = .03323 for cis decalin.

This evidence, then, along with that obtained from the graph, is sufficient to show that changes occur on heating, and that these changes are accompanied by a certain amount of irreversibility.

To investigate further the effect of heat, fresh samples of pure cis decalin were employed and treated by the following scheme:

1. Apparatus heated to 70°C.   Readings checked with previous readings at this temperature.

   Apparatus cooled to 20°C.   Readings checked with previous readings at this temperature.

2. Apparatus heated to 100°C.   Readings checked with previous readings at this temperature.

   Apparatus cooled to 20° C.   Readings checked with previous readings at this temperature.

3. Apparatus heated to 120°C.   Readings checked with previous readings at this temperature.

   Apparatus cooled to 70° C.   Readings for density and viscosity checked with previous readings but in surface tension apparatus H had increased to 1.326 cms.

4. Apparatus heated to 130°C.   Readings checked with previous readings at this temperature.

   Apparatus cooled to 70° C.   Readings for density and viscosity checked with previous readings but in surface tension apparatus H had increased to 1.336 cms.

5. Apparatus heated to 140°C.   Readings checked with previous readings at this temperature.

   Apparatus heated to 160°C.   Readings checked with previous readings at this temperature.

   Apparatus cooled to 70° C.   Readings for density and viscosity checked with previous readings but in surface tension apparatus H remained at 1.336 cms.

   Apparatus cooled to 20° C.   Readings for density and viscosity checked with previous readings but in surface tension apparatus H had changed to 1.534 cms.

With respect to the above results, it will be noted that no changes in surface tension (which appears to be more sensitive than either density or viscosity) were observed until after the decalin had been subjected to 120° C. Now the graph indicates that a radical

change occurs in the region 50° - 60° C. Since no changes were observed on cooling to 20° C. even after the heating to 100° C., we are thus led to the conclusion that whatever happens around 50° - 60° C. is reversible. The ease of reversibility is apparently great, as the cooling was accomplished quickly. The possibility that the abrupt change at 50° - 60° C. may have been due to some change in the apparatus, may be discredited, as all readings made in the heating to 70°, 100°, 120°, 130°, 140° and 160° in the above check test (using fresh decalin) duplicated the previous readings.

The heat treatment at 120° and 130° produced a change in the surface tension at 70° C. and 20° C., no further change being effected by higher heating. This apparently indicates transition in the region 120° - 130° C. Since the readings at 120°, 130° and higher temperatures checked with previous readings, and since the time of heating was fairly short, it may be concluded that the forward action of this transition is rapid. The backward action, as the cooling shows, is incomplete, for at 20° C. H now possessed the value of 1.534 cms which corresponds to γ = 32.50, or an increase of .99% over the true value for cis decalin. The increase at 20°C. in the previous readings was, as stated, 2.30%. However, since the check test was done in much shorter time than were the previous observations, it would appear that the longer the heat treatment, the greater is the tendency to produce irreversibility.

II. A Study of the Plotted Results for the Physical Properties of Trans Decalin.

The accompanying graph shows the effect of temperature on the physical properties of trans decalin. As in the case of the cis form, examination of the curves reveals characteristic breaks, again

Graph Showing Variation with Temperature
of Surface Tension, Density & Viscosity of
Trans Decalin
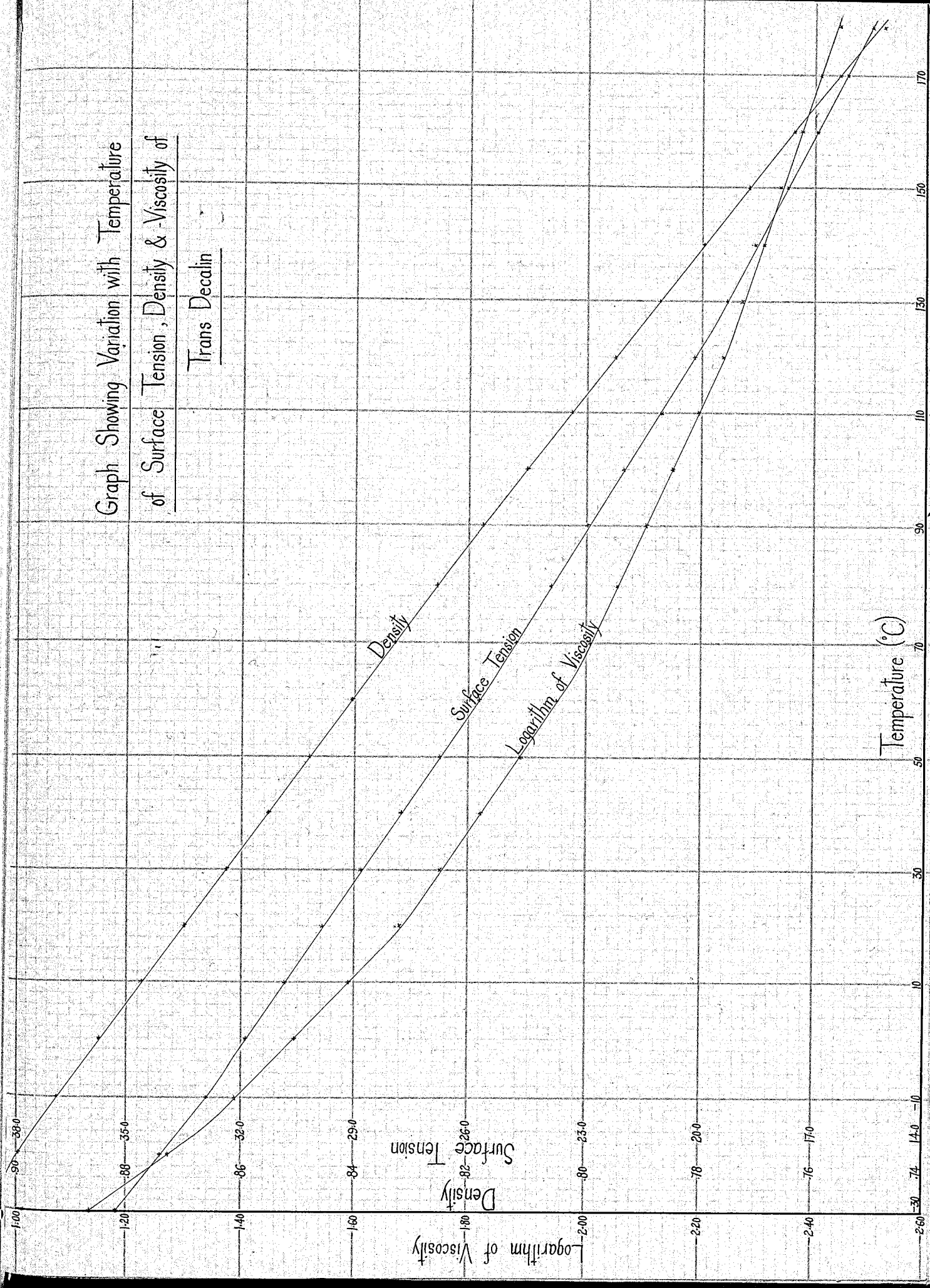
indicating possible transitions. It will be noticed that the curve for surface tension is linear but shows breaks at $-10°$ - $0°$ C., $50°$ - $60°$ C., and $120°$ - $130°$ C.; the curve for density is linear but falls off rapidly beyond $80°$ C.; the curve for logarithm of viscosity is linear but shows four breaks at approximate temperatures of $-10°$ to $-15°$ C.; $10°$ - $20°$ C.; $60°$ - $70°$ C.; $120°$ - $130°$ C.

. No change was observed in the physical properties of trans decalin at $20°$ C. after the cooling down to $-30°$ C. Hence, regarding the cooling treatment, the same conclusions may be drawn for trans as for cis.

Following the heat treatment to $180°$ C., the physical properties were again measured at $20°$ C. However, unlike the case for cis decalin no changes were observed for trans. This would then point to the fact that any transitions in structure produced by heating trans decalin (the graphs show that such transitions must occur) are totally unstable at lower temperatures; that is, the reactions are reversible.

As a brief summary we may now say that:

(1) between $-10°$ and $0°$C., a completely reversible reaction occurs for both isomers.

(2) between $50°$ and $60°$C., a completely reversible reaction occurs for both isomers.

(3) between $120°$ and $130°$C., a reaction occurs, completely reversible for trans, but not so for cis.

III. The Variation with Temperature of Density.

The effect of temperature on the linear characteristics of the D_t^4 v.s. $t°$ relationship has been previously mentioned. For

cis decalin, the linear section ranges from -30°C. to 130°C. and is given fairly well by

$$D_t^4 = .9120 - .000752 t$$

Deviations from this equation do not exceed .02%
For trans decalin, the linear relationship ranges from -30°C. to 80°C. and is well represented by

$$D_t^4 = .8849 - .000742 t$$

Deviations from this equation do not exceed .01%. The inclusion of square terms in an attempt to extend these equations over the whole temperature range studied, was found to be unsatisfactory.

As a means of getting approximate values for the critical densities of the two isomers, the law of Cailletet and Mathias was investigated. The accompanying table and graphs illustrate the manner of procedure. Values of "d" (saturated vapor density) were calculated from the ideal gas law, using vapor pressures previously determined by Nemetz and Henniker[1]. On plotting average density against temperature, the usual straight lines were obtained. For cis, the line is well given by

$$\frac{D_t^4 + d_t^4}{2} = .4560 - .000376 t$$

Deviations from this equation do not exceed .02%
and for trans by

$$\frac{D_t^4 + d_t^4}{2} = .4424 - .000368 t$$

Deviations from this equation do not exceed .01%
From the work on surface tension (see page 39) we may take the critical temperatures of cis and trans as 428°C. and 410°C. respectively. On substituting in the above equations (or extrapolating), we thus obtain a critical density of .2950 for cis and .2915 for trans. Since the data show the line for trans to fall off gradually at the higher temperatures, it is probable that the critical density of trans is lower than .2915, possibly around .2880.

....

1. Nemetz, H. and Henniker, C., M.A. Sc. and B.A. Sc. respectively
Thesis (1938).

Data Involved in Plotting the Law of Cailletet and Mathias.

Temperature ($^\circ$C)	for cis			for trans		
	D_t^4	d_t^4	$\dfrac{D_t^4 + d_t^4}{2}$	D_t^4	d_t^4	$\dfrac{D_t^4 + d_t^4}{2}$
-30	.9350	0	.4675	.9072	0	.4536
-20	.9274	0	.4637	.8997	0	.4498
-10	.9196	0	.4598	.8922	0	.4461
0	.9120	0	.4560	.8849	0	.4424
10	.9044	0	.4522	.8775	0	.4387
20	.8967	0	.4483	.8700	0	.4350
30	.8892	.0001	.4446	.8627	.0001	.4314
40	.8817	.0001	.4409	.8553	.0001	.4277
50	.8742	.0001	.4371	.8480	.0001	.4240
60	.8667	.0001	.4334	.8405	.0003	.4204
70	.8592	.0001	.4296	.8331	.0004	.4167
80	.8519	.0002	.4260	.8255	.0006	.4130
90	.8442	.0003	.4222	.8178	.0008	.4093
100	.8368	.0003	.4185	.8104	.0009	.4056
110	.8294	.0005	.4149	.8025	.0011	.4018
120	.8218	.0007	.4112	.7952	.0012	.3982
130	.8144	.0008	.4076	.7876	.0016	.3946
140	.8066	.0011	.4038	.7798	.0018	.3908
150	.7986	.0014	.4000	.7717	.0022	.3869
160	.7906	.0018	.3962	.7638	.0026	.3832
170	.7825	.0022	.3923	.7555	.0029	.3792
180	.7745	.0028	.3886	.7474	.0035	.3754

Graph Showing Application of
Law of Cailletet and Mathias
to Isomers of Decalin

Temperature (°C)

Average Density $\left(\dfrac{D_{\frac{t}{4}} + d_{\frac{t}{4}}}{2}\right)$

cis t_c

trans t_c

cis

trans
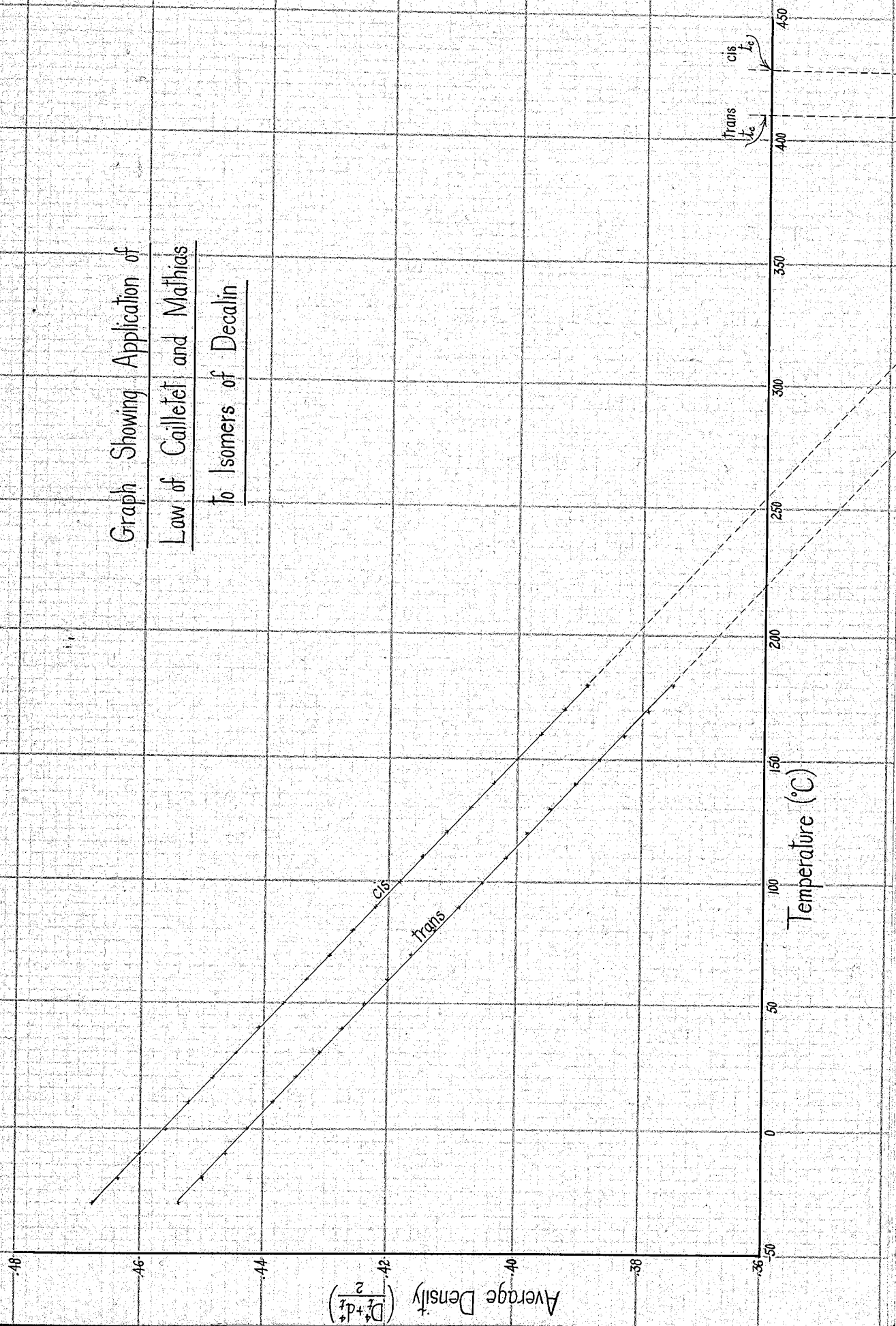
As a means of getting approximate values for the critical pressures, we cannot use the ideal gas law due to the high pressures involved, but we may make use of the equation of corresponding states

$$\left(\pi + \frac{3}{\phi^2} \right)(3\phi - 1) = 8\theta$$

In this equation $\pi = \dfrac{Pt}{Pc}$, $\phi = \dfrac{Vt}{Vc} = \dfrac{dc}{dt}$ and $\theta = \dfrac{Tt}{Tc}$.

Employing the values of $dc = .2950$ for cis and $dc = .2880$ for trans; partial pressures at 100°C. of $P_{100} = 5.821$ cms. for cis and $P_{100} = 16.041$ cms. for trans; and calcualting d_{100} from the ideal gas law, we find that Pc is equal to 46.1 and 45.0 atmospheres for cis and trans respectively.

IV. The Variation with Temperature of Surface Tension.

As previously stated the curves for surface tension are linear but show characteristic breaks. For cis decalin, the conditions are well represented by:

(a) $\gamma = 34.50 - .1162\, t$ which holds from -30°C. to 50°C.

(b) $\gamma = 33.24 - .0920\, t$ which holds from 60°C. to 120°C.

(c) $\gamma = 32.24 - .0835\, t$ which holds from 130°C. to 180°C.

Deviations in equation (a) do not exceed .09% and in equations (b) and (c) do not exceed .1%.

For trans decalin, we have the following:

(a) $\gamma = 31.78 - .1170\, t$ which holds from -30°C. to -10°C.

(b) $\gamma = 31.91 - .1020\, t$ which holds from 0°C. to 50°C.

(c) $\gamma = 31.39 - .0930\, t$ which holds from 60°C. to 120°C.

(d) $\gamma = 30.33 - .0835\, t$ which holds from 130°C. to 180°C.

Deviations in equations (a) and (b) do not exceed .09% and in equations (c) and (d) do not exceed .4% and .1% respectively.

As a means of getting an approximate value for the critical temperature of each of the two isomers, the Eötvös equation was

employed, this being given by

$$\gamma(Mv)^{\frac{2}{3}} = k(t_c - t - 6).$$

Since this equation contains two unknowns, k and tc, it was necessary to use pairs of temperatures to effect a solution. The relation holds strictly for the higher temperatures but in order to show what happens at lower temperatures, the accompanying table shows calcualtions covering the whole temperature range. The following is a brief summary:

1. for cis decalin

(a) from -30°C. to 50°C., average k = 2.83 and average tc = 353.3° C.

(b) from 60°C. to 180°C., average k = 2.24 and average tc = 428.6° C.

(c) assuming Guldberg-Guye law, $T_c = \frac{3}{2}T_b$, to hold, and taking boiling point of cis as 193°C., we get

$$t_c = \frac{3}{2}(273 + 193) - 273 = 426°C.$$

This is in good agreement with results given in (b)

2. for trans decalin

(a) from -30°C. to 50°C., average k = 2.51 and average tc = 374.5° C.

(b) from 60°C. to 180°C., average k = 2.24 and average tc = 409.5° C.

(c) assuming Guldberg-Guye law to hold and taking boiling point of trans as 185°C; we get

$$t_c = \frac{3}{2}(273 + 185) - 273 = 414°C.$$

This is in good agreement with result given in (b).

The value, k = 2.24, for Eötvös constant, is normal and the same for both cis and trans; since it is not abnormally low, no association

Calculations of Critical Temperature and Eötvös Constant

Pair of Temperatures (^{o}C)	cis Value of t_c (^{o}C)	Value of k	trans Value of t_c (^{o}C)	Value of k
-20, -30	356.4	2.79	343.1	2.74
-10, 0	363.0	2.74	376.4	2.50
-10, 20	363.1	2.74	383.1	2.45
-10, 30	358.6	2.78	380.8	2.47
-30, 50	352.3	2.82	363.7	2.60
0, 20	359.3	2.77	383.1	2.45
0, 30	355.1	2.81	380.8	2.47
10, 20	348.6	2.87	396.4	2.37
20, 30	348.5	2.87	369.3	2.55
30, 40	340.1	2.95	358.5	2.64
40, 50	341.7	2.93	359.0	2.63
50, 60	410.8	2.36	388.6	2.40
60, 80	436.9	2.19	393.7	2.36
50, 100	424.5	2.27	385.3	2.42
70, 90	418.6	2.31	403.7	2.29
70, 100	418.5	2.31	389.0	2.39
80, 120	420.1	2.30	384.1	2.44
110, 120	429.0	2.24	411.7	2.20
110, 130	425.8	2.26	413.8	2.19
90, 140	428.4	2.25	401.1	2.31
130, 140	449.0	2.09	449.0	1.94
120, 150	441.7	2.15	428.7	2.08
120, 170	433.7	2.20	416.4	2.17
130, 160	440.4	2.15	418.1	2.15
130, 180	432.3	2.21	420.7	2.13
60, 180	428.9	2.24	405.8	2.28
150, 160	422.4	2.30	393.3	2.39
160, 170	426.0	2.27	414.1	2.19

occurs at the higher temperatures.

With the purpose of obtaining further confirmation of the above results for critical temperature, Ferguson's equation[1] was next investigated. This is of the form

$$\gamma_t = \gamma_0(1 - at)^n$$

where "a" and "n" are constants. On differentiating, we obtain the straight line equation

$$\gamma_t \left(\frac{dt}{d\gamma_t} \right) = \frac{t}{n} - \frac{1}{an}$$

We would thus expect that at the critical temperature, where $\gamma_t = 0$, $\frac{t}{n} - \frac{1}{an} = 0$, from which $tc = \frac{1}{a}$.

The accompanying table gives the necessary calculations and the graphs show the result of plotting $\gamma_t \left(\frac{dt}{d\gamma_t} \right)$ v.s. t. Since the graphs are by no means regular, no attempt was made to determine tc from any one portion of them. However, it will be noted that the plot for cis is approximately linear in three sections, and the breaks occur in the previously mentioned ranges of -10° - 0°C., 50° - 60°C., and 120° - 130°C. The plot for trans appears a little more complex. The characteristic changes at -10° - 0°C., 50° - 60°C. and 120° - 130°C. are quite evident, but in addition there are breaks at 80°C and 100°C.

V. Determination of Parachors.

Calculations of parachors were carried out employing Sugden's[2] equation

$$P = \frac{M}{D_t^4 - d_t^4} \gamma^{.25}$$

....

1. "Surface Tension and Surface Energy" by R. S. Willows & E. Hatschek (3rd ed.) 43-44.
2. Sugden, J. chem. Soc., 125, 1177 (1924).

Data and Calculations Involved in Plotting Ferguson's Equation.

Temperature Range (t = 20°C.)	Mean t (°C)	cis				trans			
		$\Delta\gamma$ in this Range	$\dfrac{dt}{d\gamma_t}$	γ_t at mean t	$\gamma_t\left(\dfrac{dt}{d\gamma_t}\right)$	$\Delta\gamma$ in this Range	$\dfrac{dt}{d\gamma_t}$	γ_t at mean t	$\gamma_t\left(\dfrac{dt}{d\gamma_t}\right)$
-30 to -10	-20	2.37	8.44	36.83	311.0	2.34	8.54	34.14	291.5
-20 to 0	-10	2.33	8.58	35.65	306.0	2.23	8.97	32.95	295.5
-10 to +10	0	2.29	8.73	34.50	301.5	2.08	9.61	31.91	307.0
0 to 20	10	2.32	8.62	33.36	287.5	2.02	9.90	30.87	305.5
10 to 30	20	2.35	8.50	32.18	273.5	2.00	10.00	29.89	298.9
20 to 40	30	2.37	8.44	31.01	262.0	2.08	9.61	28.87	278.0
30 to 50	40	2.38	8.40	29.81	250.5	2.10	9.53	27.81	265.0
40 to 60	50	2.14	9.34	28.63	267.5	1.99	10.05	26.77	269.0
50 to 70	60	1.81	11.05	27.67	306.0	1.95	10.26	25.82	265.0
60 to 80	70	1.79	11.18	26.82	300.0	1.87	10.70	24.82	265.5
70 to 90	80	1.87	10.70	25.88	277.0	1.80	11.10	23.95	266.0
80 to 100	90	1.84	10.88	24.95	271.5	1.93	10.37	23.02	238.5
90 to 110	100	1.81	11.05	24.04	265.5	1.97	10.15	22.02	224.0
100 to 120	110	1.79	11.18	23.14	258.5	1.80	11.10	21.05	234.00
110 to 130	120	1.76	11.35	22.25	253.0	1.66	12.05	20.22	243.5
120 to 140	130	1.69	11.83	21.38	253.0	1.57	12.74	19.39	247.0
130 to 150	140	1.62	12.35	20.56	253.5	1.54	13.00	18.65	242.0
140 to 160	150	1.67	11.98	19.76	236.5	1.67	11.95	17.85	214.0
150 to 170	160	1.72	11.62	18.89	219.5	1.68	11.90	16.98	202.0
160 to 180	170	1.71	11.70	18.04	211.0	1.54	13.00	16.17	210.0

Graph Showing Ferguson's Equation

Applied to the Isomers of Decalin

Temperature (°C)

Values of $\lambda_t \left(\dfrac{d\lambda_t}{dt} \right)$

trans

cis
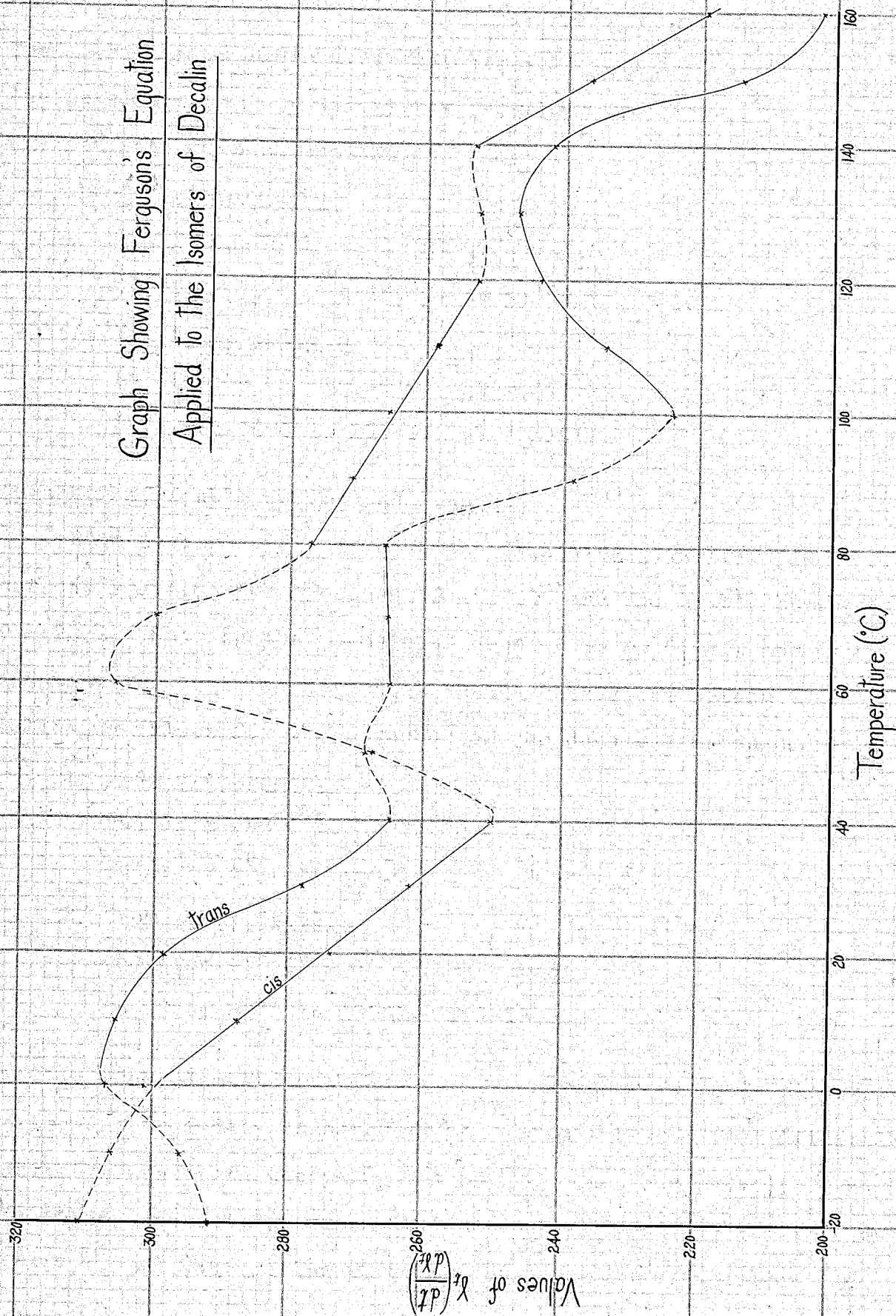
The accompanying table gives the necessary data and calculations. The results show that we may take averages for each isomer over two separate temperature ranges, thus:

1. for cis decalin

   (a) from -30°C. to 30°C, P = 366.9

   (b) from 40°C. to 160°C, P = 365.6

2. for trans decalin

   (a) from -30°C to 40°C, P = 371.1

   (b) from 50°C to 150°C, P = 369.7

Parachor of Double 6-Membered Ring.

From Sugden's work we have the following parachors: for carbon, P = 4.8; for hydrogen, P = 17.1; and for double bond P = 23.2. Knowing the formula of decalin to be $C_{10}H_{18}$ and assuming the additive nature of the parachors, we obtain the following values for the parachor of the double 6-membered ring:

1. from cis decalin

   (a) from -30°C to 30°C, P = 11.1

   (b) from 40°C to 160°C, P = 9.8

2. from trans decalin

   (a) from -30°C to 40°C, P = 15.3

   (b) from 50°C to 150°C, P = 13.9

As a supplement to this work, the parachor for this structure was worked out from data on naphthalene. From International Critical Tables we are given the values at 80.2°C. (melting point): D^4 = .9779, γ = 32.26, and P = 7.5 mms. The calculated parachor from this data is 312.1. On subtracting parachors due to carbon, hydrogen and

Data and Calculations of Parachors

Temperature (°C)	cis γ_t	D_t^4	d_t^4	Parachor	trans γ_t	D_t^4	d_t^4	Parachor
-30.00	38.02	.9350	0	366.9	35.29	.9072	0	371.1
-20.00	36.83	.9274	0	366.9	34.14	.8997	0	371.1
-10.00	35.65	.9196	0	367.1	32.95	.8922	0	371.0
0.00	34.50	.9120	0	367.1	31.91	.8849	0	371.0
10.00	33.36	.9044	0	367.1	30.87	.8775	0	371.1
20.00	32.18	.8967	0	366.9	29.89	.8700	0	371.3
30.00	31.01	.8892	.0001	366.6	28.87	.8627	.0001	371.2
40.00	29.81	.8817	.0001	366.1	27.81	.8553	.0001	370.9
50.00	28.63	.8742	.0001	365.6	26.77	.8480	.0001	370.6
60.00	27.67	.8667	.0001	365.6	25.82	.8405	.0003	370.6
70.00	26.82	.8592	.0001	365.9	24.82	.8331	.0004	370.3
80.00	25.88	.8519	.0002	365.8	23.95	.8255	.0006	370.5
90.00	24.95	.8442	.0003	365.8	23.02	.8178	.0008	370.4
100.00	24.04	.8368	.0003	365.7	22.02	.8104	.0009	369.7
110.00	23.14	.8294	.0005	365.5	21.05	.8025	.0011	369.2
120.00	22.25	.8218	.0007	365.4	20.22	.7952	.0012	368.9
130.00	21.38	.8144	.0008	365.1	19.39	.7876	.0016	368.8
140.00	30.56	.8066	.0011	365.2	18.65	.7798	.0018	369.0
150.00	19.76	.7986	.0014	365.3	17.85	.7717	.0022	369.0
160.00	18.89	.7906	.0018	365.1	16.98	.7638	.0026	368.4
170.00	18.04	.7825	.0022	364.9	16.17	.7555	.0029	368.1
180.00	17.18	.7745	.0028	364.4	15.44	.7474	.0035	368.1

double bonds we obtain P = 11.3 for that of the double 6-membered ring
This agrees fairly well with the parachor from cis decalin from
-30°C to 30°C., indicating a similarity in configuration.

As stated, the value P = 23.2 for the double bond, is used
in the calculations. It may be mentioned, however, that since a
double bond possesses modified properties in a 6-element ring to
what it possesses in say ethylene, we may not be justified in
assuming the parachor the same for both cases.

Parachor of Single 6-Membered Ring.

For this, Sugden gives the value P = 6.1. Since this was,
no doubt, obtained from data on benzene (unsaturated), it was of
interest to see if the same result would be obtained from data
on Cyclohexane (saturated). From International Critical Tables we
are given the values at 20°C. : D^4 = .7790, γ = 25.30, and
P = 76.9 mms. The calculated parachor from this data is 242.2.
On subtracting parachors due to carbon and hydrogen we obtain
P = 8.2 for that of the single 6-element ring. This differs
considerably from Sugden's value, and, as with the double ring,
is probably due to some effect of the double bonds.

VI. The Total and Molecular Surface Energies.

The accompanying table shows the calculations of total surface
energy, where total surface energy = $\gamma + T(\frac{d\gamma}{dt})$. The value of
$\frac{d\gamma}{dt}$ (really $\frac{\Delta\gamma}{\Delta t}$) was obtained by taking Δt = 10°C and getting
corresponding values of $\Delta\gamma$. The following is a brief summary
of the results:

1. for cis decalin

(a) from -30°C to 50°C, average $\frac{d\gamma}{dt}$ = .117 and average total
surface energy = 66.44 ergs.

Data and Calculations of Total and Molecular Surface Energies.

Temperature (°C)	cis γt	cis Δγ	cis Total Surface Energy (ergs)	cis Molecular Surface Energy (ergs)	trans γt	trans Δγ	trans Total Surface Energy (ergs)	trans Molecular Surface Energy (ergs)
-30.00	38.02		66.45	1062.6	35.29		61.05	1006.3
		1.19				1.15		
-20.00	36.83		66.43	1034.9	34.14		60.96	978.9
		1.18				1.19		
-10.00	35.65		66.42	1007.4	32.95		60.83	950.1
		1.15				1.04		
0.00	34.50		66.44	980.3	31.91		60.85	925.1
		1.14				1.04		
10.00	33.36		66.47	953.2	30.87		60.87	900.0
		1.18				.98		
20.00	32.18		66.46	924.7	29.89		60.95	876.4
		1.17				1.02		
30.00	31.01		66.46	896.2	28.87		60.99	851.3
		1.20				1.06		
40.00	29.81		66.43	866.4	27.81		60.99	824.8
		1.18				1.04		
50.00	28.63		66.42	836.8	26.77		61.01	798.5
		.96				.95		
60.00	27.67		56.97	813.4	25.82		57.45	774.7
		.85				1.00		
70.00	26.82		57.00	793.0	24.82		57.40	749.1
		.94				.87		
80.00	25.88		56.94	769.6	23.95		57.48	727.3
		.93				.93		
90.00	24.95		56.89	746.4	23.02		57.50	703.4
		.91				1.00		
100.00	24.04		56.86	723.4	22.02		57.45	677.0
		.90				.97		
110.00	23.14		56.84	700.5	21.05		57.43	651.4
		.89				.83		
120.00	22.25		56.83	677.7	20.22		51.66	629.5
		.87				.83		
130.00	21.38		56.84	655.1	19.39		51.63	607.6
		.82				.74		
140.00	20.56		56.90	634.1	18.65		51.69	588.3
		.80				.80		
150.00	19.76		56.98	613.5	17.85		51.69	567.0
		.87				.87		
160.00	18.89		56.99	590.4	16.98		51.62	543.0
		.85				.81		
170.00	18.04		57.02	567.7	16.17		51.61	520.9
		.86				.73		
180.00	17.18		57.04	544.4	15.44		51.68	501.0

(b) from 60°C to 180°C, average $\frac{d\gamma}{dt}$ = .088 and average total surface energy = 56.92 ergs.

2. **for trans decalin**

    (a) from -30°C to 50°C, average $\frac{d\gamma}{dt}$ = .106 and average total surface energy = 60.94 ergs.

    (b) from 60°C to 110°C, average $\frac{d\gamma}{dt}$ = .095 and average total surface energy = 57.45 ergs.

    (c) from 120°C to 180°C, average $\frac{d\gamma}{dt}$ = .080 and average total surface energy = 51.65 ergs.

It will be noted that the agreement between values of total surface energies for different temperatures in any one temperature range, is very good.

The values of molecular surface energy (the $\gamma(Mv)^{\frac{2}{3}}$ of the Eötvös equation) are tabulated and the variation with temperature is shown on the accompanying graph. The curves are linear, and, as might be expected, are very similar to those for γ v.s. t. The characteristic breaks are again evident, those for both isomers showing up at 50° - 60°C and 120° - 130°C.

VII   The Latent Heats of Vaporization and Fusion.

As a means of getting an approximate value for the latent heat of vaporization, the work of Walden[1] was investigated. We have the equation:

$$\frac{(\Delta H_v)(D_b^4)}{\gamma_b} = 3.64$$

where ΔH_v = latent heat of vaporization per gram
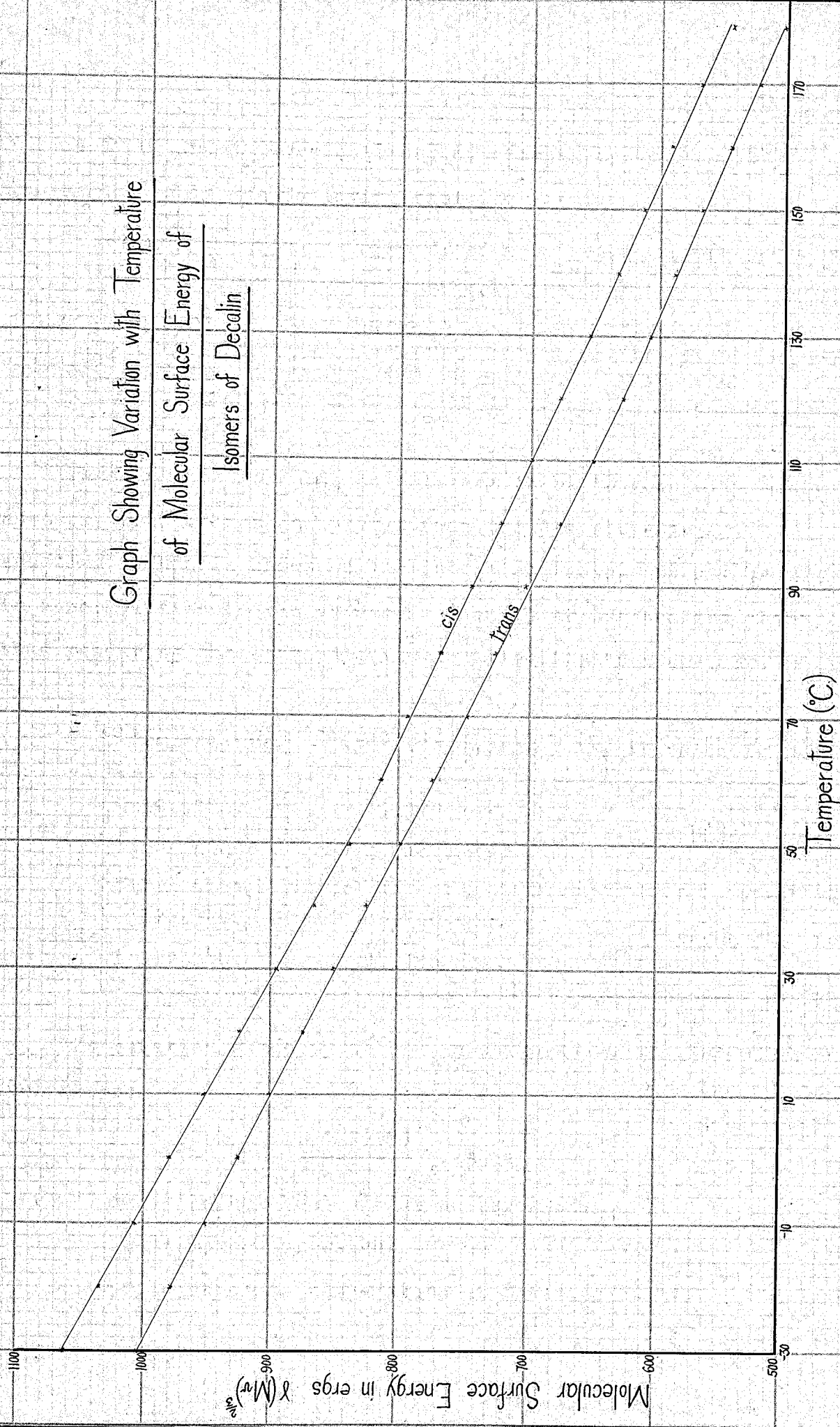
    D_b^4 = density of liquid at boiling point

    γ_b = surface tension of liquid at boiling point

....

1. "Surface Tension and Surface Energy" by R. S. Willows & E. Hatschek (3rd ed.) 41-42.

Graph Showing Variation with Temperature
of Molecular Surface Energy of
Isomers of Decalin

Temperature (°C.)

Molecular Surface Energy in ergs $\gamma (M_v)^{2/3}$

cis

trans

Values of D_b^4 and γ_b were obtained by extrapolation, and ΔH_v determined as in the following table:

	γ_b	D_b^4	ΔH_v in calories per gr.
cis	16.05	.7638	76.5
trans	14.99	.7433	73.4

These values for ΔH_v do not seem to be in good agreement, however, with values calculated from the Clausius-Clapeyron equation. This is shown in the following table, and may be due to abnormalities in the values of γ and D at the boiling point, thus rendering the extrapolation an illegitimate procedure.

	Temperature	Vapor Pressure	ΔH_v in calories per gr.
cis	191.7°C.	74.276 cms.	91.0
	202.6°C.	101.47 cms.	
trans	171.3°C.	59.710 cms.	54.9
	187.3°C.	80.485 cms.	

The equation given by Walden, and involving the latent heat of fusion, is:

$$\frac{(\Delta H_f)(M)}{T_f} = 13.14$$

where ΔH_f = latent heat of fusion per gram

M = molecular weight

T_f = absolute temperature at freezing point.

The following table shows the calculated values:

	Freezing point (^{o}C)	ΔH_f in calories per gr.
cis	-43.26^{o}	21.8
trans	-31.49^{o}	23.0

VIII   The Variation with Temperature of Viscosity.

The graph of u v.s. t was drawn for each isomer, and the curves obtained appear perfectly regular and normal in shape. However, when log u is plotted against $\frac{1}{t}$ (or, as shown on the accompanying graphs, when log u is plotted against t--giving a curve form which is similar to the other but concave to the right), we obtain for each isomer a curve which is made up of five different straight lines. The transition temperatures from one line to another have been mentioned (see sections 1 and 2). Now it will be recalled that five isomeric forms for decalin have been postulated by Wightman. It may be possible, then, that these five forms are represented by this simple viscosity-temperature relationship.

Data for the viscosity of benzene[1] were next obtained and were plotted similarly against $\frac{1}{t}$. The resulting curve is made of two linear portions, the change from one to the other being in the region 30° - 40°C. Since the values of Eötvös constant are not abnormally low for either benzene, or the isomers of decalin, such changes in slope cannot be attributed to changes in association,

. . . .

1. J. Phy. Chem. 34. 1599-1606.

but apparently are due to alterations in the molecular configuration.

To investigate further this evidence from viscosity, and to link up the viscosity with other physical data, the work of Batschinski[1] was examined. He proposes the relation

$$\frac{1}{u} = c(v - a)$$

where a and c are constants and v = specific volume.

Hence

$$\frac{1}{u} = \frac{C}{D} - ac$$

a straight line for $\frac{1}{u}$ v.s. $\frac{1}{D}$.

The plots for this equation are shown on the accompanying graph. It will be noticed that the curve for cis is really made up of four straight lines separated at temperatures of $-10^{\circ} - 0^{\circ}$, $30^{\circ} - 40^{\circ}$ and $80^{\circ} - 90^{\circ}$; the curve for trans is composed of three straight lines separated at temperatures of $0^{\circ} - 10^{\circ}$ and $50^{\circ} - 60^{\circ}$. These transition temperatures do not agree very well with those previously given, and no indication is given of any change near 120°; however, the parallelism of the curves is quite marked, and the fact that linear characteristics are shown, proves the applicability of Batschinski's relation.

. . . .

1. Batschinski, A., Zeit. physik. Chem., 84, 643 (1913).

Calculations Involved for the Plot of Batschinski's Equation.

Temperature (°C)	cis		trans	
	$\dfrac{1}{u_t}$	$\dfrac{1}{D^4_t}$	$\dfrac{1}{u_t}$	$\dfrac{1}{D^4_t}$
-30.00	6.55	1.069	13.70	1.102
-20.00	9.22	1.078	18.71	1.111
-10.00	13.55	1.087	24.50	1.121
0.00	18.28	1.096	31.24	1.130
10.00	23.95	1.106	38.90	1.140
20.00	30.09	1.115	47.17	1.149
30.00	37.33	1.125	56.02	1.159
40.00	45.21	1.134	66.27	1.169
50.00	54.02	1.144	77.52	1.179
60.00	63.65	1.154	89.37	1.190
70.00	73.64	1.164	101.42	1.200
80.00	83.26	1.173	114.02	1.211
90.00	94.79	1.184	127.06	1.223
100.00	107.91	1.195	141.44	1.234
110.00	121.03	1.206	156.99	1.246
120.00	134.79	1.217	173.01	1.258
130.00	148.26	1.228	186.56	1.270
140.00	163.48	1.240	204.08	1.282
150.00	178.19	1.252	217.87	1.296
160.00	194.33	1.265	236.97	1.309
170.00	210.04	1.278	257.73	1.324
180.00	227.38	1.291	277.01	1.338

Graph Showing Batschinski's Equation

Applied to the Isomers of Decalin

Values of $\frac{1}{\mu}$

Values of $\frac{1}{D}$

Cis

Trans
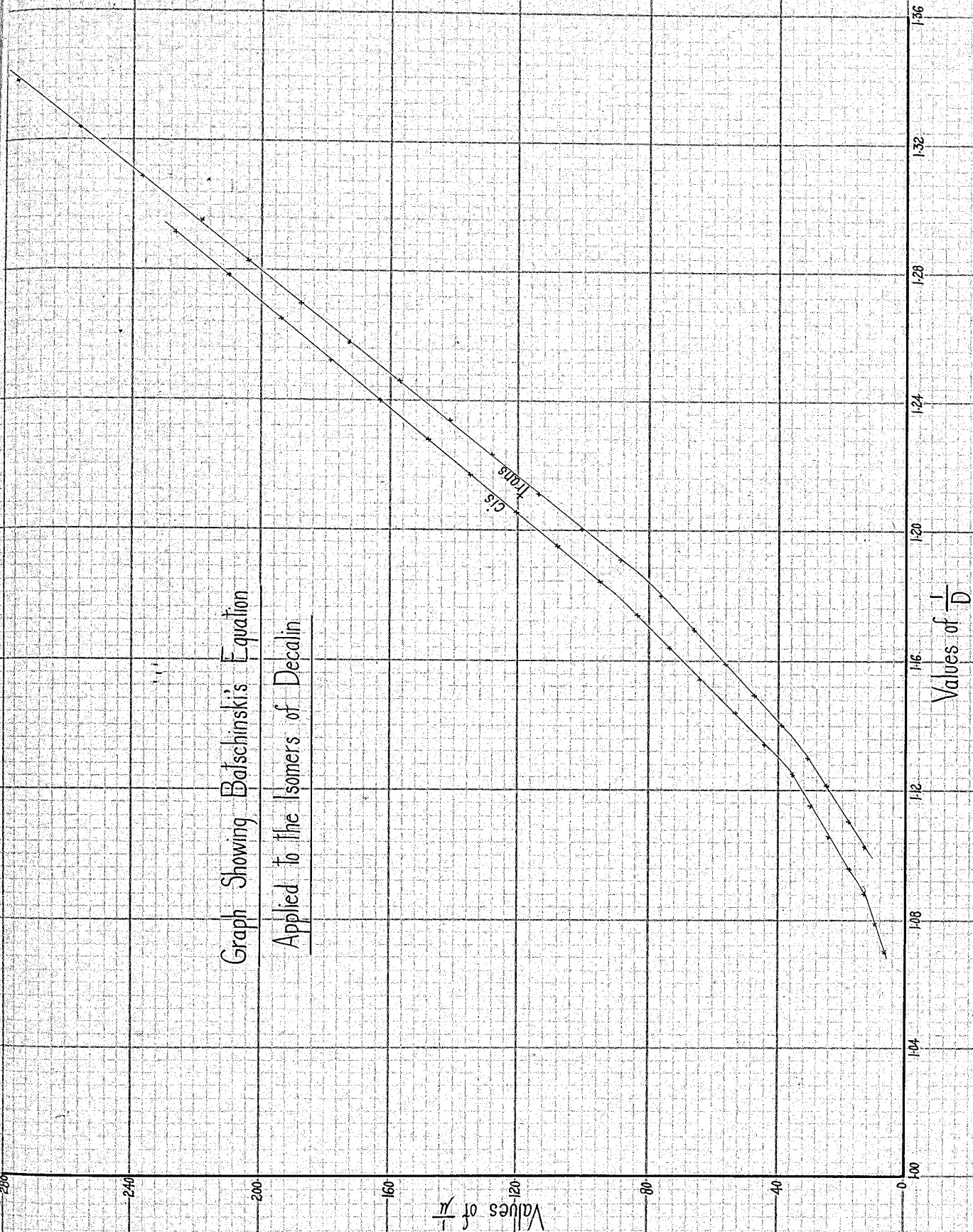
PART IV

Information Obtained from Further Rectification and Crystallization.

In order to secure more of each pure isomer for subsequent research, it was decided to follow again the regular procedure of rectification and crystallization. Commencing with the raw, unwashed decalin, the method was precisely the same as previously described. Since, however, rather large yields were obtained, certain difficulties were encountered (chiefly in the crystallization treatments) and it is for this reason, and in order to present several conclusions that this work has been presented in some detail.

1. Results of the Rectification of Cis and Trans Decalin.

Rectification No. 1   September 26--October 1, 1938.

Characteristics of Charge:

(a) 2000 c.c. of Eastman Kodak decalin.

(b) $D_{20}^{4} = .8875$

(c) $N_{20}^{D} = 1.47834$

(d) approximate composition = 24.5% trans.

	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
Boiling Point of Fraction (°C)	59.0-59.5	59.5-61.2	61.2-64.3	64.3-66.4	66.4-67.9
Volume of Fraction (c.c.)	200	227	331	225	528
Time for Fraction (hrs.)	13.5	14.5	23.0	20.0	50.5
Rate of Fractionation (c.c./hr)	14.8	15.6	14.4	11.25	10.5
Index of Refraction (N^{D})	1.46983	1.46993	1.47255	1.47975	1.48118
Approximate Composition (% cis)	1.9	2.2	25.6	88.1	>100

Final residue in column bulb = 400 c.c.

Hence total loss during rectification = 89 c.c.

Rectification No. 2　　　　　　　October 6--October 13, 1938.

Characteristics of Charge:

(a) 2378 c.c. of decalin, comprising 1475 c.c. of raw
Eastman Kodak decalin + 400 c.c. of bottoms of
Rectification No. 1 + 330 c.c. of bulb 3
Rectification No. 1 + 173 c.c. of 84% trans
decalin from 1937 runs.

(b) D_{20}^{4} = .8890

(c) N_{20}^{D} = 1.47849

(d) approximate composition = 23% trans

	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
Boiling Point of Fraction (°C)	59.5-60.2	60.2-62.0	62.0-64.9	64.9-67.8	67.8-68.7
Volume of Fraction (c.c.)	370	500	345	405	280
Time for Fraction (hrs.)	24.5	33.0	30.5	42.5	29.0
Rate of Fractionation (c.c./hr)	15.1	15.1	11.3	9.5	9.6
Index of Refraction (N_{20}^{D})	1.46988	1.47081	1.47804	1.48123	1.48128
Approximate Composition (% cis)	2.0	11.2	73.2	>100	>100

Final residue in column bulb = 440 c.c.

Hence total loss during rectification = 38 c.c.

Rectification No. 3   October 21--October 28, 1938.

Characteristics of Charge:

(a) 2053 c.c. of high cis decalin comprising bulb 5 of
Rectification No. 1; bulbs 4 and 5 of Rectification
No. 2; and 840 c.c. of high cis decalin from the
crystallization treatments of 1937-38.

(b) D_{20}^{4} = .8965

(c) N_{20}^{D} = 1.48118

(d) approximate composition = 100% cis.

Boiling Point of Fraction (°C)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
	67.1-67.6	67.6-68.0	68.0-68.6	68.3-68.8	68.5-68.7
Volume of Fraction (c.c.)	100	330	725	370	160
Time for Fraction (hrs.)	10.0	32.0	74.5	38.5	17.0
Rate of Fractionation (c.c./hr)	10.0	10.3	9.7	9.6	9.4
Index of Refraction (N_{20}^{D})	1.48044	1.48108	1.48108	1.48108	1.48108
Approximate Composition (% cis)	93.0	100	100	100	100

Final residue in column bulb = 240 C.c.

Hence total loss during rectification = 128 c.c.

It appears from the above that practically all the impurities were
concentrated in bulb 1, and that the remaining bulbs contained cis
decalin of very high purity.

Before proceeding with the trans, the column was now washed
thoroughly by refluxing in it for 5-6 hours a charge of decalin which
had an approximate composition of 70% trans. This washing charge was
made up of two fractions obtained from the R. D. Walker--W. F. Seyer
rectifications.

Rectification No. 4   November 3--November 9, 1938.

Characteristics of Charge:

(a) 1950 C.c. of high trans decalin, comprising bulbs
    1 and 2 of Rectification No. 1; bulbs 1 and 2 of
    Rectification No. 2; and 653 c.c. of high trans
    decalin from the crystallization treatments of 1937-38.

(b) D_{20}^4 = .8700

(c) N_{20}^D = 1.47008

(d) approximate composition = 96.6% trans.

Boiling Point of Fraction (°C)	Bulb 1	Bulb 2	Bulb 3	Bulb 4	Bulb 5
	59.0-61.0	61.0-61.7	61.6-62.3	62.3-61.5	61.5-61.0
Volume of Fraction (c.c.)	85	378	460	220	360
Time for Fraction (hrs.)	6.5	30.0	43.0	23.5	34.5
Rate of Fractionation (c.c./hr)	13.1	12.6	10.7	9.4	10.4
Index of Refraction (N_{20}^D)	1.46889	1.46933	1.46938	1.46933	1.46943
Approximate Composition (% trans)	>100	100	100	100	100

Final residue in column bulb = 390 c.c.

Hence total loss during rectification = 57 c.c.

The above table shows that the chief impurities in our trans

concentrates were of the low-boiling point type. Their removal

appears to have been done quite efficiently, for bulbs 2,3,4 and 5

are of the same approximate composition.

2. The Final Purification of Cis and Trans Decalin by Fractional Crystallization.

(a) Apparatus and Experimental Procedure. Except for minor changes, everything was the same as in the previous work. In the case of the cis, it was found that the crystallizations could be well done by placing our decalin in an 800 c.c. glass Dewar (using an air wall), and cooling the whole with solid carbon dioxide in a much larger Dewar. Hand stirring was employed throughout and no trouble with supercooling was encountered. However, for trans it was necessary to evacuate the 800 c.c. Dewar in order to reduce to a minimum the rate of heat transfer. Also, to reduce heat transfer still further, it was necessary to use mechanical stirring, since its use allowed the formation of a thick layer of crystals on the sides of the Dewar. Such treatment favored the phenomenon of supercooling, but no difficulty was experienced as seeding was employed.

(b) Experimental Results for Cis Decalin. The fractions selected for the purification were bulbs 2,3,4 and 5 of Rectification No. 3. Using a combination of bulbs 2,4 and one-half of bulb 5, it was found that eight separate crystallizations were required to obtain the pure isomer and that the volumetric yield was 530 c.c. As before the product was dried using metallic sodium. For this material, our final result is:

$$F.P. = -43.29 \pm .04^{\circ}C. \text{ and } N_{20}^{D} = 1.48113$$

The purification treatment as applied to a combination of bulb 3 and the remaining half of bulb 5, gave very interesting

results. After five crystallizations, the material could not be purified further and gave a constant F. P. = -43.08°C. This result was obtained approximately three weeks after the fractionation of the high cis decalin by Rectification No. 3. Ten days after the determination of this freezing point, another test was run on the same material. This showed the constant freezing point to have fallen now to -43.14°C. Again, two months later, another test indicated the freezing point to be still -43.14°C. The volumetric yield of this material was 590 c.c.

This work on cis decalin clearly suggests the presence of some unstable form of cis isomer. Its presence, predominately in bulb 3, appears quite remarkable, none-the-less fortunate, and its concentration may be attributed to careful rectification. As stated above, our first measurement on this sample was made about three weeks after Rectification No. 3. Hence, concerning further investigation along this line, it seems plausible to suggest that, following careful rectification of cis decalin, freezing point determinations should be commenced as soon as possible with the separate fractions.

(c) <u>Experimental Results for Trans Decalin</u>. As mentioned previously, several precautions had to be taken in order to obtain optimum conditions for the crystallization of trans decalin. Many trial runs were made to investigate different effects, and it was finally concluded that, when a dry ice cooling medium is employed, the use of mechanical stirring and a well evacuated Dewar (10^3 - 10^4 mms.), are necessary. Further, it was demonstrated that hand stirring produces the same freezing point as mechanical stirring, but in the former case the rate of cooling is much greater due to the crystals

forming within the bulk of the liquid and not being swept to the sides of the flask.

Using a combination of bulbs 4, 5 and one-half of bulb 3, all of Rectification No. 4, it was found that six separate crystallizations were required to obtain the pure isomer and that the volumetric yield was 500 c.c. However, using bulb 2 and the other half of bulb 3, twenty crystallizations were required to obtain the constant point, and the volumetric yield was 135 c.c. The freezing points of the two batches agreed. For trans decalin, our final result is:

F. P. = -31.16 $\pm$ .04°C.   and N_{20}^{D} = 1.46954

PART V.

A Study of the Effect of Heat on the Decomposition of Cis and Trans Decalin.

That heat produced decomposition in the isomers of decalin seemed apparent from the discovery of the presence of unsaturateds in the heat-treated liquids which had undergone the measurements of density, surface tension and viscosity. In the case of the cis liquid the reduction of alkaline potassium permangamate was quite rapid; in the case of the trans liquid the reduction was also observed but the time required was much longer than for the cis. In both cases, the refractive index remained that of the pure isomer--one instance of the fact that refractive index is not a sensitive physical property of these isomers. It would appear from this, then, that at the higher temperatures cis and trans decalin tend to revert to the unsaturated compounds from which they were formed; and that the tendency to do so is much greater for cis than for trans. Since hydrogen would be given off in such a reaction, it is quite possible that vapour pressures read too high when hydrogen is present, but on the other hand it is possible that this may be compensated by the lowering in vapour pressure from the solution of the unsaturated compound in the pure decalin. A slight divergence from the true values may also be expected in those obtained for density, surface tension and viscosity at the elevated temperatures, and it is interesting to note that it may be this divergence which is responsible for the slight falling off in the curves at the higher temperatures. Experimental verification of the formation of unsaturateds again is indicated, this time in

the data obtained for cis. As the author's work shows, the heat treatment resulted in the cis liquid having a higher density, surface tension and viscosity at 20°C. than the pure cis possesses. This would indicate a partial change at least of the saturated configuration of pure cis to that of an unsaturated, for a study of the data on the unsaturated double ring (naphthalene) indicates its physical properties to be higher than those of the saturated (as pure cis or trans).

To investigate more fully the amount of structural change undergone, it was decided to follow the production of unsaturateds by following the change in iodine number. It is quite possible that the following results do not indicate unsaturation only, as some substitution may always take place during the absorption. This substitution would be retarded by the use of low temperatures. However, since differences only were desired, absorption at 20°C. was deemed sufficiently accurate for the purpose, and all measurements were reproducible.

(a) The Experimental Procedure.   The method employed was essentially that due to Hübl with the important modification suggested by Wijs[1]. Two litres of glacial acetic acid were distilled twice in the presence of potassium permanganate in order to oxidize any alcohol or acetaldehyde. The first 50 c.c. of each distillate was rejected. This done, about 6.5 grams of pure iodine were dissolved in the purified acid, and then washed and dried chlorine was passed into the solution until the color changed from dark brown to reddish yellow. That this color change occurred when the titer of the solution was just double that of the initial iodine solution,

....

1. Sutton, "Volumetric Analysis", 10th edition, page 412-415.

was shown by titrations with standard sodium thiosulphate on
the initial iodine and final chlorinated solutions. The standard
thiosulphate was prepared by Volhard's method. Chloroform was
used as solvent for the decalin; also used in the titrations
were a 10% solution of potassium iodide and a freshly-prepared
1% starch solution. Each titration was done in a 250 c.c., clean,
Pyrex flask possessing a well-ground glass stopper.

In making a determination, a weighed sample of the decalin
(about .8 grams) was placed in the flask, dissolved in 10 c.c. of
chloroform, and 20 c.c. of the iodine monochloride solution added.
The flask was corked and shaken well and allowed to stand for 2 hours
in the dark, after which time 10 c.c. of potassium iodide solution
and 100 c.c. of water were added. In order to prevent loss of
iodine by volatilization, the liquids were allowed to run around
the wide-lipped neck about the stopper, which was partially removed
to allow the solution to enter the flask. The excess iodine was
titrated with sodium thiosulphate, using starch indicator at the end.

The preparation of the decalin samples was done in the following
manner. About twenty small tubes, each with a 2-3 c.c. bulb on the
end, were prepared. After thorough cleaning a small amount of pure,
dry decalin was introduced into each bulb. The samples were then
frozen in a "dry ice" medium and while in this condition the tubes
were blown on to a series of T-tubes extending vertically outwards
from a mother tube. By connecting one end of the mother tube to a
vacuum pump, the whole could be evacuated. This done, the decalin
was unfrozen under vacuum to remove dissolved air, and then hydrogen
was admitted to the apparatus. Finally, the decalin was once again
frozen, the whole re-evacuated, and the series of tubes sealed off

under vacuum.

The heat treatment of the various samples was done employing a small constant-temperature bath, equipped with thermometer, stirrer and thermostatic mechanism.

(b) <u>Results of the Heat Treatments</u>. Prior to the heating, analyses of the pure cis and trans isomers prepared in 1937-38, indicated for each an apparent iodine number of .08 whereas for the pure isomers prepared in 1938-39 the number was .04. These small iodine numbers may be attributed to substitution. In confirmation of the results obtained with alkaline potassium permanganate, analysis of the heat-treated cis and trans liquids from 1938 indicated apparent iodine numbers of .36 and .15 respectively.

Heat treatment of the decalin samples in the evacuated tubes failed to produce any unsaturated compounds. Thus, using the pure decalin prepared in 1937-38, the iodine number remained .08 even after 20 hours heating at 170°C. and 6 hours heating at 200°C. Tests were carried out at 170°C. with open tubes and it was found that although small amounts of unsaturation were produced, the results were not reproducible for different tubes. Slight discolorations in some of the tubes indicated that the change in iodine number could be attributed to minute amounts of oil getting into the tubes from the hot oil bath.

The above work on heat treatment serves to clarify several results obtained in this research on decalin:

1. The iodine numbers found to exist for the heat-treated cis and trans liquids of 1938, were probably due to slight amounts of

oil vapor getting into the open density tube (viscometer and surface tension tube were closed). Oxidation may have been responsible for part of the change.

2. Irreversible structural changes without the formation of unsaturateds must occur for cis decalin at elevated temperatures. This evidence is obtained from the changes which occured in the closed viscometer and surface tension tube. As noted in previous conclusions, such changes for trans are reversible.

3. The results indicate that if unsaturateds are formed from cis and trans decalin at temperatures up to 200°C. in closed tubes, the reactions are reversible on cooling.

Bibliography

1. Mohr, J. Phys. Chem., 98, 315 (1918)   103, 316 (1922).

2. Wightman, J. Chem. Soc., 127, 1421 (1925).

3. Willstatter & Seitz, Berichte, 57B., 683-4 (1924)

4. Zelinsky, N. O. & Turova-Pollak, M. B., Berichte, 58B.,
        1292-98 (1925).

5. Huckel, W., Annalen der Chemie, 441, 1 (1925).

6. Herz, Z. Physik. Chem. 101, 269 (1922).

7. Kirk, L. M., B. A. Sc., Thesis (1935).

8. Manley, D., B. A. Sc., Thesis (1934).

9. Cornett, W. F., B. A. Sc., Thesis (1935).

10. Walker, R. D., M. A. Sc., Thesis (1937).

11. Seyer, W. F., Associate Professor in Chemistry, University of B. C.

12. Richards, Speyers & Carver; J. Am. Chem. Soc., 46, 1196 (1924).

13. Bennett, R., B. A. Sc., Thesis (1935).

14. Nemetz, H. & Henniker, C., M. A. Sc. & B. A. Sc., Thesis
        respectively (1938).

15. Willows, R. S. & Hatschek, E., "Surface Tension and Surface Energy"
        (3rd ed.), 41-44.

16. Sugden, J. Chem. Soc., 125, 1177 (1924).

17. Batschinski, A., Z. Physik. Chem., 84, 643 (1913).

18. Sutton, "Volumetric Analysis", 10th ed., p. 412-415.