INVESTIGATION OF THE SPECIFIC HEAT OF CIS DECAHYDRONAPHTHALENE

by

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CONTENTS

ILLUSTRATIONS

Separation of the Pure Cis and Trans Isomers of Decahydronaphthalene.

Introduction.

Under the direction of Dr. W.F. Seyer considerable work has been done on the problem of separating and determining the properties of the isomeric forms of decahydronaphthalene. It is thought that decahydronaphthalene exists in 5 stereo-isomeric forms, the cis and trans forms being the limiting positions of the other three and therefore of greater stability.

The first successful separation was accomplished in 1936-37 by Dr. W.F. Seyer and R.D. Walker.(1) In 1937-38 another successful separation was carried out by L. Gould, H. Nemetz, C. Davenport, and J. Henniker.(2)

The object of the following research was to separate more cis and trans decahydronaphthalene and to construct an apparatus for the determination of the temperature coefficients of the specific heats of the cis and trans isomers.

Preparation.

Commercial decalin from the Eastman Kodak Co. was

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

(2) Gould, L.R. M.A.Sc. Thesis, 1938.

used. The two isomers were separated by repeated rectification followed by fraction crystallization. The apparatus and method used was that used by R.D. Walker.

The results of the rectification and crystallization are as follows.

Rectification # 1.

Charge 2000 c.c. E.K. decalin D^4 0.8875 N 1.48734 Comp. 24.5% T

Results.

	Bulb 1.	Bulb 2.	Bulb 3.	Bulb 4.	Bulb 5.
Vol.	200 c.c.	227 c.c.	331 c.c.	225 c.c.	528 c.c.
N	1.46983	1.46993	1.47255	1.47975	1.48118
Comp.	98.1% T	97.8% T	25.6% C	88.1% C	100% C

Bottoms 400 c.c.

Rectification # 2.

Charge 1475 c.c. E.K. dec. as of 1. & 400 c.c. bottoms from 1. & 173 c.c. bulb 4. run 1(a) Trans last yr. & 330 c.c. of R.1. B.3 this yr. N 1.47849 D 0.886 Comp. 23% T.

Results.

	Bulb 1.	Bulb 2.	Bulb 3.	Bulb 4.	Bulb 5.
Vol.	370 c.c.	500 c.c.	345 c.c.	405 c.c.	280 c.c.
N	1.46988	1.47081	1.47804	1.48123	1.48121
Comp.	98% T	88.8% T	73.7% C	100% C	100% C

Bottoms 440 c.c.

Rectification # 3.

Charge 2053 c.c. high cis R.1. B.5.; R.2. B.4. & 5. & 840 c.c. of last year. N 1.48118 D 0.8965 Comp. 100% C

Results.

	Bulb 1.	Bulb 2.	Bulb 3.	Bulb 4.	Bulb 5.
Vol.	100 c.c.	330 c.c.	725 c.c.	370 c.c.	160 c.c.
N	1.48044	1.48108	1.48108	1.48108	1.48108
Comp.	93% C	100% C	100% C	100% C	100% C

Bottoms 240 c.c.

Rectification # 4. High Trans.

Charge R.1. B.1. & 2. & fractions from last year. Vol. 1950 c.c.
N 1.47008 D 0.8700

Results.

	Bulb 1.	Bulb 2.	Bulb 3.	Bulb 4.	Bulb 5.
Vol.	85 c.c.	378 c.c.	460 c.c.	220 c.c.	360 c.c.
N		1.46933	1.46938	1.46933	1.46943

Bottoms 390 c.c.

Crystallizations.

Cis. Bulb 2. & 4. & half of 5.
9 crystallizations - freezing point -43.29°C.

Bulbs 3. & half of 5.
6 crystallizations - High F.P. allowed to stand several months to effect structural changes. Re-run F.P. after -43.14°C.

Trans.
20 crystallizations - freezing point -31.16°C.

Summary of Results.

Isomer	Freezing Point °C		D_{20}
Cis	-43.29°C	0.2	1.48113
Trans	-31.16°C	0.2	1.46968

Specific Heat Calorimeter.

Since it was desired not only to determine the specific heat of decahydronaphthalene but also the temperature coefficient of the specific heat it was necessary to use a method of measuring the absorption of heat over a small temperature range.

The adiabatic method of Richards (1) and of Williams and Daniells (2) was considered the best for the purpose.

A strictly adiabatic method was necessary in order to prevent evaporation of the liquid and to prevent all transference of heat to the cold room. A calorimeter was built according to the specifications of Williams and Daniells.

In brief the method entails the measurement of the quantity of electricity and the time required to raise the temperature of a known weight of liquid through a given temperature interval.

Apparatus.

The apparatus used is illustrated in Fig. 1.

The liquid to be measured was contained in a cylindrical copper vessel (A) 8 cm. high and 6 cm. in

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(1) Richards: J. Am. Chem. Soc. 31, 1275 (1909).

(2) J.W.Williams & F. Daniells: J. Am. Chem. Soc. 46, 904 (1924).

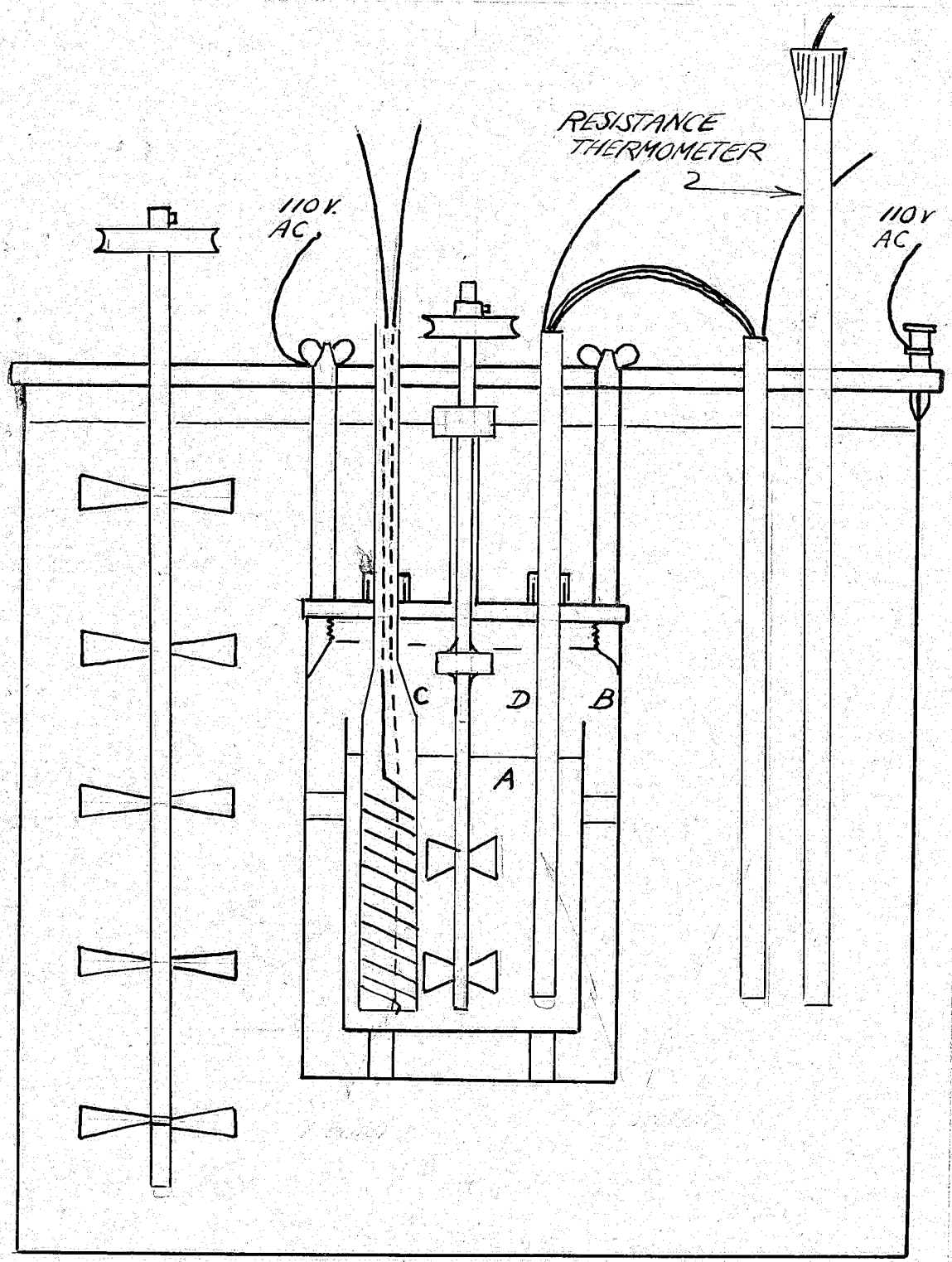


DIAGRAM OF CALORIMETER

Fig. 1.

diameter held in place by insulated supports in an enclosing vessel with an air gap of 7 mm. between the two.

The enclosing vessel (B) was also of copper 12 cm. high and 8 cm. in diameter fitted with a threaded cover of bronze. A flat rubber ring was used as a gasket between the cover and the vessel to prevent leakage. A little grease was also applied to the threads.

The cover was provided with an upright tube for the stirrer and with stuffing boxes for the admission of the heater (C) and the thermocouple (D). The inner stirrer was of brass and attached to the main shaft by asbestos board to prevent thermal contact between the liquid and the outer bath. A cap attached to the upper shaft rotated in the liquid of the outer bath so as to make a seal and to prevent the movement of air. Such a precaution was necessary to prevent the evaporation of some of the liquid due to air currents.

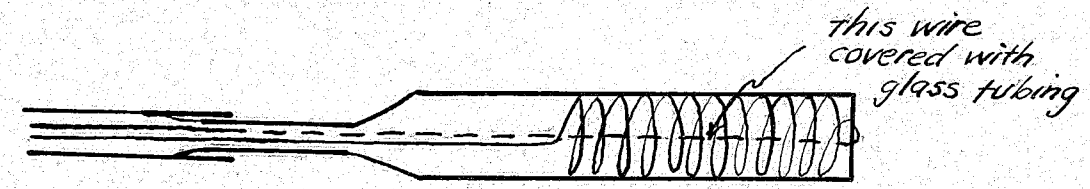
The multiple thermal of 5 copper-constantan thermocouples was enclosed in a thin glass tube and connected with a sensitive galvanometer. Oil in the tube gave quicker response to temperature changes in the bath.

The thermal was constructed as follows:
The pairs of wires were cut off and bared of insulation for 2 or 3 mm. at each end and soldered together. The wire used was size 32. Each junction was then insulated by dipping separately into a fairly thick rubber solution consisting of pure gum rubber dissolved in a mixture of

benzene and carbon disulphide. The rubber was then allowed to set by heating moderately (about 100°).

Two sets of five thermocouples were made and the wires were joined together in two halves with four lead wires, by means of which the two halves may be connected either in series or in opposition. Hence to test the thermals no deflection should occur when they are in opposition with one end at room temperature and the other in ice water. The wires were made into a compact bundle by binding with silk thread and then enclosed in the glass tube. Enclosing the thermocouples presented difficulties. It was found almost impossible to insert the thermal in a "Y" tube without breaking the lead wires. An "h" tube was then tried but usage caused either breakage of the wire or glass. The type shown in the diagram proved satisfactory. The tubes were completely filled with oil so that rapid heat transfer from the glycerine to the thermal wires would prevent conduction of heat from the inner liquid along the wires.

The heater was constructed by winding resistance wire around a flat piece of mica as shown below.



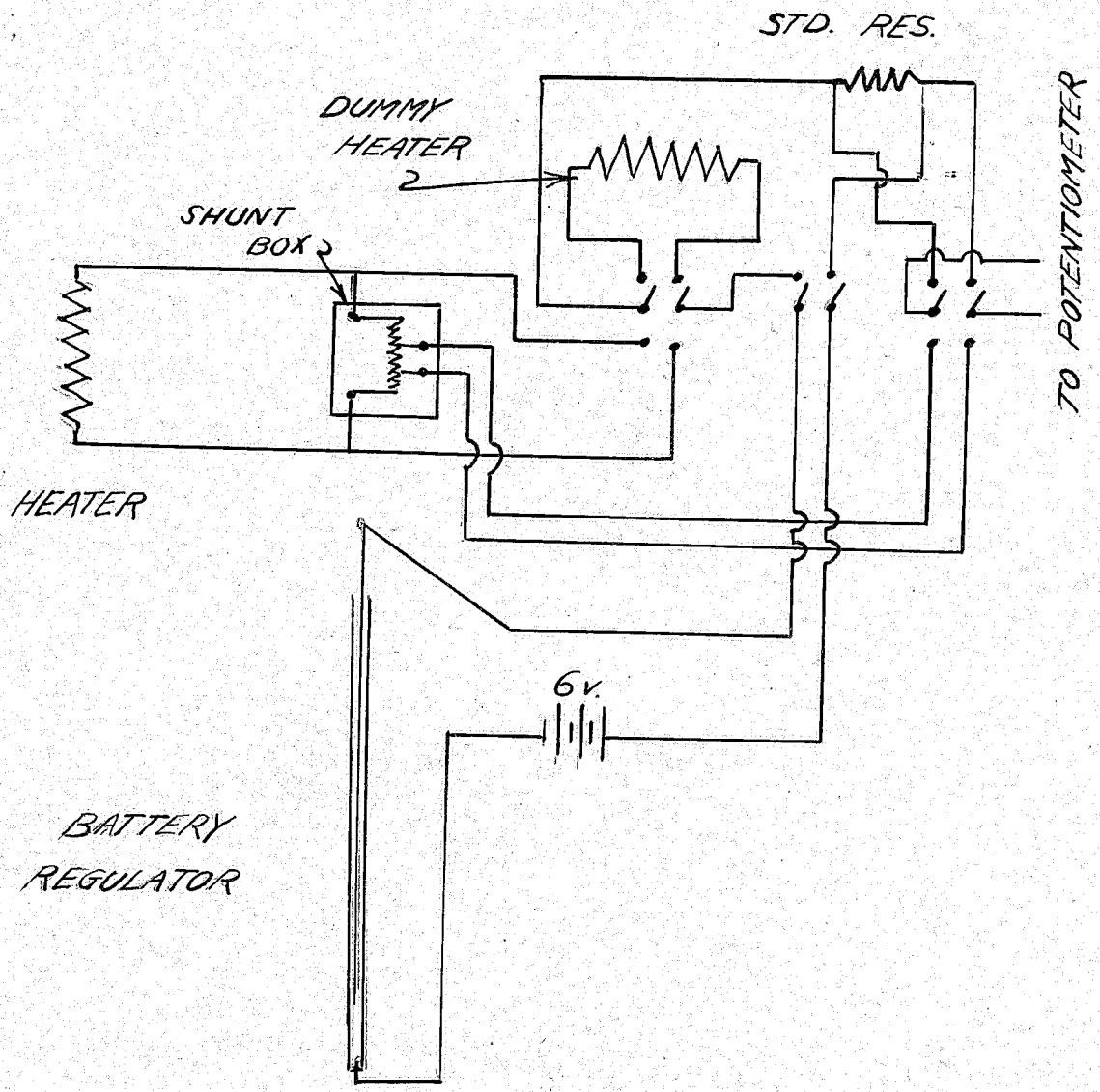
The resistance of the heater was about 20 ohms for the working conditions followed.

It was found necessary to use rubber insulated wires for the heater leads to prevent short-circuit through the copper tubing. Of course any part of the wire that was immersed in the organic liquid had to be free of insulation. Also complete immersion of the heating element was required.

The temperatures were measured with a platinum resistance thermometer and a high precision bridge.

Williams and Daniells found that the transference of heat along a platinum resistance thermometer from the inner calorimeter to the room amounted to as much as 0.35 calories per minute when the calorimeter was 15° above the temperature of the room even though the whole upper part of the thermometer was immersed in the outer bath at the same temperature as the inner. This difficulty was eliminated by placing the thermometer in the outer bath where no measured heat losses can occur. The readings on the resistance thermometer were taken only when the thermal galvanometer registered zero.

The tank for the outer bath was constructed of sheet copper. It was packed in asbestos contained in a still larger can. The bath contained 9 litres of glycerol in which was dissolved 20g. of ferric chloride to make it an electrolytic conductor. It was heated externally with resistance wire wound around the tank and internally by passage of an alternating current directly through the liquid bath from



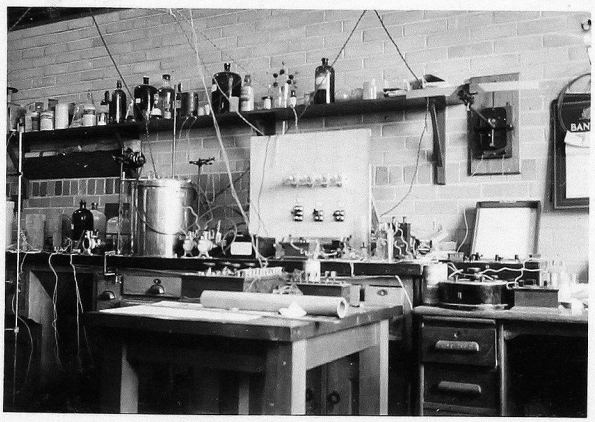
-BATTERY CIRCUIT-

Fig. 2.

the insulated calorimeter to the tank. A rheostat in the external heating circuit allowed efficient temperature control. The alternating current aided by a motor d riven stirrer provided adequate agitation of the glycerine. Although the copper sides of the bath were being heated externally the temperature of the glycerine was only about one half a degree less than that of the wall.

The current for the inner heater was supplied by a 6 volt storage battery. The electrical circuit is shown in Fig. 2.

The potential difference across the heater was measured with a sensitive potentiometer, the voltage being reduced through a shunt box to a convenient quantity for measurement. The current through the heater was measured by the potential drop across a 1 ohm standard resistance.



ASSEMBLY

Procedure.

A given volume (155 c.c.) of the liquid to be investigated was accurately weighed and introduced into the calorimeter. Measured amounts of electrical energy were passed through the heater for definite time intervals. The heating of the outer bath was regulated so as to keep the thermel always on zero thus ensuring adiabatic control.

A single sample of liquid was used for the entire temperature range.

The following procedure for the recording of observations was necessary in order that the apparatus could be controlled by one person.

1. The heating circuit was closed with the dummy heater in the circuit, this being left in for 20 to 30 mins. to allow the initial high E.M.F. from the battery to come to equilibrium.

2. The current was then diverted into the real heater and the stop watch started. Adiabatic control was then commenced by observing the thermel and putting in or pulling out the two bath heating switches as required to keep the thermel on zero. Usually the electrolytic heater could be left in and the outside heater only operated.

3. The P.D. across the heater and the current through it, together with the resistance of the platinum resistance thermometer were measured and the time of measurement noted. In the case of the temperature the time had to be to the nearest second. It was found better to

leave the last deal or 4th decimal place of the resistance bridge on 0 and to take the time when a resistance reading in the 3rd decimal occurred.

In taking temperatures 3 or 4 readings were taken as close together as possible, then after the lapse of the desired time 3 or 4 more were taken also as close together as possible. This enabled a number of heat input calculations to be made about the mean temperature. Lag in recording the temperature was thus minimized.

The change in resistance for a definite interval of time was obtained by plotting R against temp. For a 5 to 10° interval a straight line resulted.

The readings of the thermometer had to be corrected for N, R, NZ, and RZ after the run.

For the sake of brevity it is inadvisable to include all the readings of each run in this paper. However, the following is a typical example of the method and readings.

Run # 22. 50°C.

Time	P.D.	Current I.	Resistance
22:47			2.9620
25:10			2.9690
26:37			2.9730
28:30			2.9780
29:00	5.7036		
00:00		0.32296	
3:15			2.9910
5:15			2.9970
7:05			3.0020
11:45			3.0150
12:30	5.7035		
14:39			3.0230
17:07			3.0300
18:38			3.0340
19:00	5.7038		
20:00		0.32294	

The accurate determination of the water equivalent of the calorimeter presented difficulty.

An approximate value was obtained by weighing or estimating the weight of the parts of the calorimeter which absorbed some of the measured heat, and then calculating the heat capacity.

Calculation of Water Equivalent.

Substance	Wt.	Sp. Ht.	Ht. Cap. G./deg.
Copper	278.1	.092	107
Glass	5.4	.165	3.7
Mica	2.9	.208	2.5
Brass	18.9	.094	7.4
Oil	.6	.5	.12
			120.77

This is only an estimate.

The water equivalent was obtained by using pure benzene and toluene in the calorimeter using data from the International Critical Tables for the respective specific heats. The results are as follows:

Benzene.

Temp.	Wt. of liquid	Sp. Ht.	Total Input	B Input	W.E.
30°C	137.26 g.	1.732 J/deg.	385	238	147
30°C	138.7	1.732	386	241	145
30°C	138.3	1.732	384	240	144
30°C	134.9	1.732	380	234	146
				Ave.	145.5

Toluene.

Temp.	Wt. of liquid	Sp. Ht.	Total Input	B Input	W.E.
30°C	135.9	1.70 J/deg.	376	231	145
30°C	135.0	1.70	373	230	143
30°C	130.5	1.70	372	222	150
30°C	137.5	1.70	375	234	141
30°C	137.4	1.70	375	234	141
				Ave.	144

These were the purest liquids obtainable of known specific heat. Since the object of the investigation was primarily that of studying the variation of specific heat with temperature rather than the absolute value of the specific heat a reference water equivalent was obtained from these figures rather than a correct water equivalent. Further investigation of the water equivalent was omitted due to pressure of time as it would have been necessary to use a pure liquid of low vapour pressure and known specific heat and no such liquid was available.

The benzene used had been recrystallized and was purer than the toluene. The average water equivalent found from the benzene runs was taken as the basic value. i.e. 145.5 joules per degree at 30°C. This is noticeably higher than the estimated water equivalent. The difference is thought to be due to heat absorbed by solder, cork, and insulating material which could not be estimated. The agreement between benzene and toluene favoured the higher value.

Using a water equivalent of 145.5 joules/degree at

30°C the specific heat of C.P. carbon tetrachloride was investigated.

Two runs were made at 30°C.

Results: 1. Sp. Ht. CCl_4 = .868 joules/deg.

2. Sp. Ht. CCl_4 = .867 joules/deg.

The value given in the critical tables = .837 joules per degree at 30°C. This again favoured a water equivalent in the neighbourhood of 145 joules/deg. In consequence a basic water equivalent 145.5 joules/deg. at 30°C was used in the subsequent decahydronaphthalene investigations.

The change in water equivalent with temperature also presented difficulty. The change in the calculated equivalent 120.77 was determined by calculating the increase for a 10° rise in temperature. This was then put on a basis of 145.5. Resulting value was an increase of .5 joules per degree for each 10 degree rise in temperature. This agreed quite well with the 0.3 joules per degree used in the original calorimeter of Williams and Daniells. It was noticed that in calibrating the instrument the graphs of temp. vs. time were parallel irrespective of the liquid used. This arises from the fact that the heat capacity per unit volume of most liquids is a constant. Approximately the same volume was used in each case.

Water was also tried as a calibration liquid but did not prove satisfactory due to corrosion of the bare heating wire. Also the high specific heat of water gave operating conditions that were not parallel with those of the organic liquids.

Observations for Cis Decahydronaphthalene.

Run # 19. Wt. of Cis 143.083 g.

Temp.	Res. Int.	Factor	1000 sec. Temp. Int.	P.D.	I.	Sp. Ht.
25°	2.7770 2.7323	1.02	4.54°	5.536	.3160	1.677
30°	2.8403 2.7961	1.02	4.51	5.5362	.3159	1.683
35°	2.8873 2.8427	1.02	4.55	5.537	.3158	1.667
40°	2.9365 2.8921	1.02	4.53	5.537	.3157	1.675
45°	2.9795 2.9353	1.02	4.51	5.538	.3156	1.687
50°	3.0155 2.9715	1.02	4.49	5.5377	.3155	1.689

Run # 20. Wt. of Cis 143.038 g.

Temp.	Res. Int.	Factor	1000 sec. Temp. Int.	P.D.	I.	Sp. Ht.
30°	2.8385 2.7910	1.02	4.845	5.7435	.32805	1.702
35°	2.8861 2.8385	1.02	4.855	5.7443	.3280	1.694
40°	2.9429 2.8957	1.02	4.814	5.7440	.32797	1.715
45°	2.9841 2.9363	1.02	4.886	5.7443	.32794	1.673
50°	3.0230 2.9753	1.02	4.865	5.7446	.32790	1.683
55°	3.0857 3.0393	1.02	4.733	5.7443	.32780	1.750
60°	3.1331 3.0873	1.03	4.717	5.7440	.32767	1.762
65°	3.1867 3.1411	1.03	4.697	5.7435	.32760	1.771
70°	3.2312 3.1860	1.04	4.701	5.744	.32755	1.766
75°	3.2852 3.2410	1.04	4.597	5.7435	.3275	1.828
80°	3.3290 3.2851	1.04	4.566	5.743	.3274	1.844

Run # 21 Wt. of Cis 141.934 g.

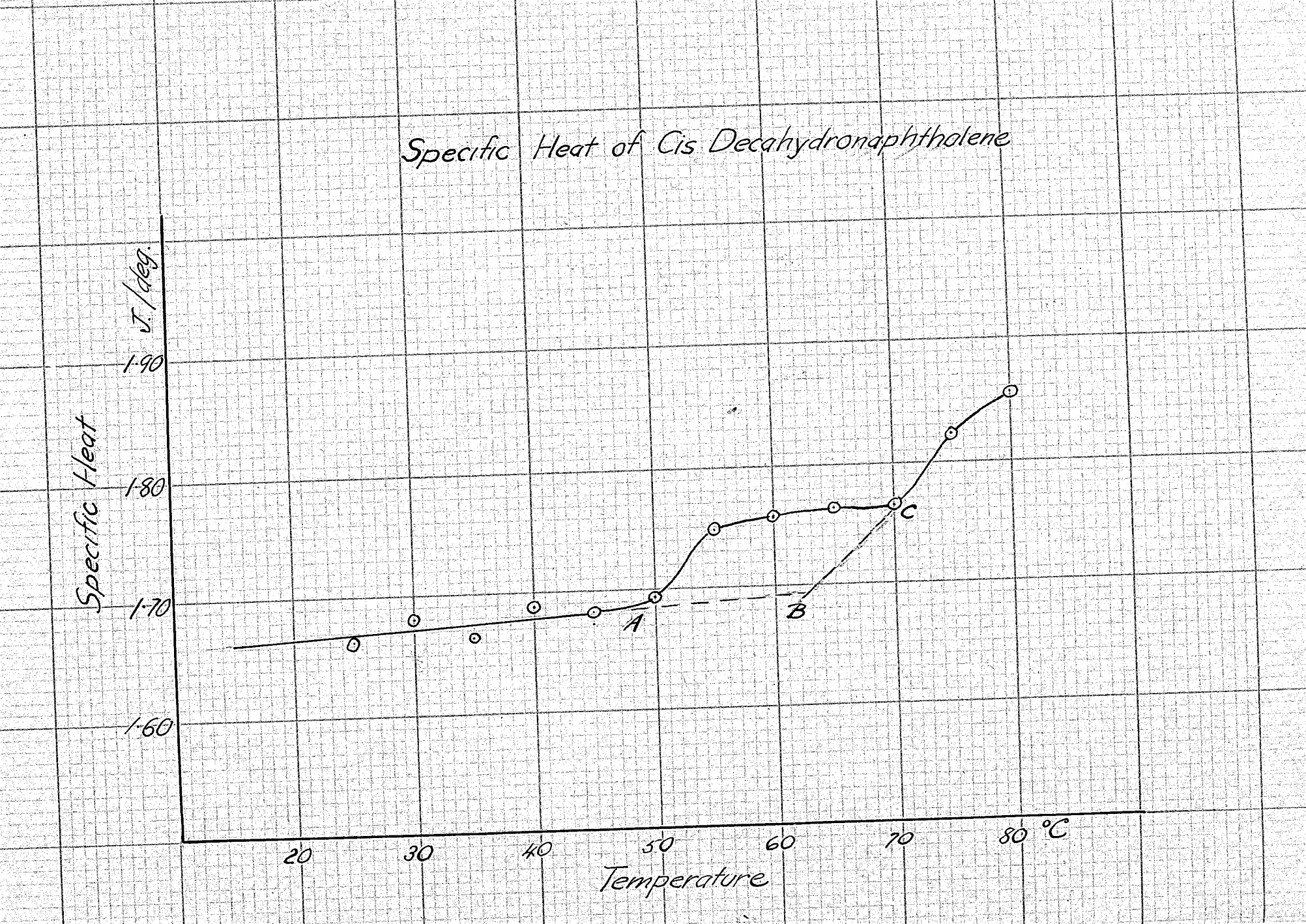
Temp.	Res. Int.	Factor	1000 sec. Temp. Int.	P.D.	I.	Sp. Ht.
30°	2.8414 2.8221	1.02	1.969 (400 s.)	5.725	.3243	1.632
35°	2.8920 2.8438	1.02	4.916	5.7267	.32435	1.635
40°	2.9390 2.8915	1.02	4.845	5.7268	.32435	1.673
45°	2.9767 2.9302	1.02	4.743	5.7260	.32425	1.737
50°	3.0119 2.9650	1.02	4.784	5.7250	.32420	1.701
55°	3.0892 3.0431	1.02	4.702	5.7240	.32415	1.746
60°	3.1354 3.0900	1.03	4.676	5.7230	.32410	1.760
65°	3.1893 3.1439	1.03	4.676	5.7225	.32400	1.758
70°	3.2266 3.1818	1.04	4.660	5.7210	.32387	1.762
75°	3.2859 3.2420	1.04	4.566	5.7204	.32385	1.818
80°	3.3232 3.2798	1.04	4.514	5.7185	.32385	1.847

Run # 22 Wt. of Cis 141.934 g.

Temp.	Res. Int.	Factor	1000 sec. Temp. Int.	P.D.	I.	Sp. Ht.
35°	2.8996 2.8518	1.02	4.876	5.705	.3232	1.637
40°	2.9371 2.8903	1.02	4.774	5.704	.3230	1.691
45°	2.9841 2.9372	1.02	4.784	5.704	.3230	1.683
50°	3.0180 2.9713	1.02	4.763	5.704	.3230	1.693
55°	3.0851 3.0396	1.02	4.671	5.704	.3229	1.750
60°	3.1244 3.0792	1.03	4.656	5.704	.3229	1.751
65°	3.1881 3.1429	1.03	4.656	5.703	.3229	1.750
	Run # 23	Wt. of Cis	141.934 g.			
25°	2.7953 2.7483	1.02	4.794	5.663	.3206	1.645
30°	2.8432 2.7960	1.02	4.814	5.663	.3206	1.702
35°	2.8880 2.8415	1.02	4.743	5.663	.3206	1.685
40°	2.9440 2.8971	1.02	4.784	5.664	.3205	1.645
45°	2.9767 2.9302	1.02	4.743	5.664	.3205	1.666
50°	3.0141 2.9681	1.02	4.692	5.664	.3205	1.694

Specific Heat in Joules per degree per gram.

Temp.	Run #19	#20	#21	#22	#23	Ave.
25°	1.677				1.645	1.661
30°	1.683	1.702	1.632		1.702	1.680
35°	1.667	1.694	1.635	1.637	1.685	1.663
40°	1.675	1.715	1.673	1.691	1.645 ×	1.689
45°	1.687	1.673	1.737 ×	1.683	1.666 ×	1.681
50°	1.689	1.683	1.701	1.693	1.694	1.692
55°		1.750	1.746	1.750		1.749.
60°		1.762	1.760	1.751		1.758
65°		1.771	1.758	1.750		1.762
70°		1.766	1.762			1.764
75°		1.828	1.818			1.823
80°		1.844	1.847			1.846


Specific Heat of Cis Decahydronaphtholene
Specific Heat
J./deg.
1·90
1·80
1·70
1·60
A
B
C
20
30
40
50
60
70
80 °C
Temperature

Conclusions.

From the data it will be noticed that the variation in the values of the specific heat below 45°C is much greater than the variation above. This may be due to sharp changes in the viscosity at low temperatures.(1) Also the lag in the absorption of heat by the various parts of the calorimeter was probably greater at lower temperatures. It was noted that the movements of the thermocouple were faster above 45 or 50° than they were below. The viscosity of the glycerine in the bath may also have had some effect on the temperature measurement due to non-uniform heating when more viscous.

The slope of the curve in the graph of Sp. Ht. vs. temp. for cis decahydronaphthalene indicates that a transition takes place in the neighbourhood of 50°C. This is to be expected from similar changes at 50° in the surface-tension-temperature curve for the cis isomer.(1)

Unfortunately the calorimeter in use, although suitable for the measurement of the total heat capacity of a liquid, was not suitable for distinguishing between the actual specific heat and the latent heat of transition.

To do this it would be necessary to build a similar apparatus, with the temperature of the inner liquid measured directly instead of by means of the thermocouple and bath thermometer. The control of the inside heater and bath

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(1) Davenport, C.H. B.A.Sc. Thesis, 1938.

heating equipment would also have to be a great deal more sensitive so that discontinuities in the temperature-time curves could be followed without superheating the decalin during transition.

Actually the transition should take place without any rise in temperature. When a large volume of liquid, as in the above case, is used it is increasingly difficult to effect transition without imparting heat to the liquid already transformed.

The Sp. Ht.-temperature curve indicates that transition started at approximately 50°C and continued to about 70°C. The area between the Sp. Ht. curve and the lines AB, BC is a measure of the heat of transition. From the graph the value of the heat of transition is about 0.85 joules per gram.

In regard to the numerical value of the Sp. Ht. the extrapolated value from the curve for 15°-18°C is 1.661 joules per degree. This compares favourably with the value 1.653 joules/degree given for cis decahydronaphthalene at 15°-18°C in the International Critical Tables.

Note: Mica as a base for winding the heating element wire proved to be unsatisfactory when used with decalin at temperatures above 80° due to capillarity effect and spreading of the mica sheets.

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