THE SECOND-ORDER PHASE TRANSITION

OF

CIS DECAHYDRONAPHTHALENE

By

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INTRODUCTION

The physical properties of cis decahydro-naphthalene have been studied extensively in this laboratory. The evidence obtained from measurements of vapour pressure (figure 1), surface tension (figure 2), and viscosity suggest the presence of a transition point in the liquid state. Dr. H. D. Smith and his assistants [18] found evidence for a Verdet constant change with temperature in the vicinity of $50^{\circ}C$, (figure 3). Smith, Barton [19] and Zotov [20] found differences in the Raman effect of the isomer at temperatures above and below $50^{\theta}C$. Surface tension measurements indicate it takes place at $50^{\circ}C. \pm 0.2^{\circ}C$.

Since no discontinuity was found in the density curve (figure 4) has been suggested the transition is of a second-order. It is the bject of the present research to determine the nature of the transition from studies of the specific heat curves.

FIG I

VARIATION OF LOG OF VAPOUR PRESSURE WITH RECIPROCAL OF TEMPERATURE FOR CIS DECAHYDRONAPHTHALENE

Caption: Variation of log of vapour pressure with reciprocal of temperature for cis decahydronaphthalene. Y-axis: Log P (1.6, 0.8, 0, -0.8). X-axis: $\frac{1}{T} \times 10^{-3}$ (2.0, 2.4, 2.8, 3.2, 3.6, 4.0).

FIG 2.

VARIATION OF SURFACE TENSION WITH TEMPERATURE FOR CIS DECAHYDRONAPHTHALENE

Caption: Variation of surface tension with temperature for cis decahydronaphthalene. Y-axis: Surface Tension - Dynes/cm. (38, 32, 26, 20). X-axis: Temperature, °C (-30, 0, 30, 60, 90, 120, 150, 18).
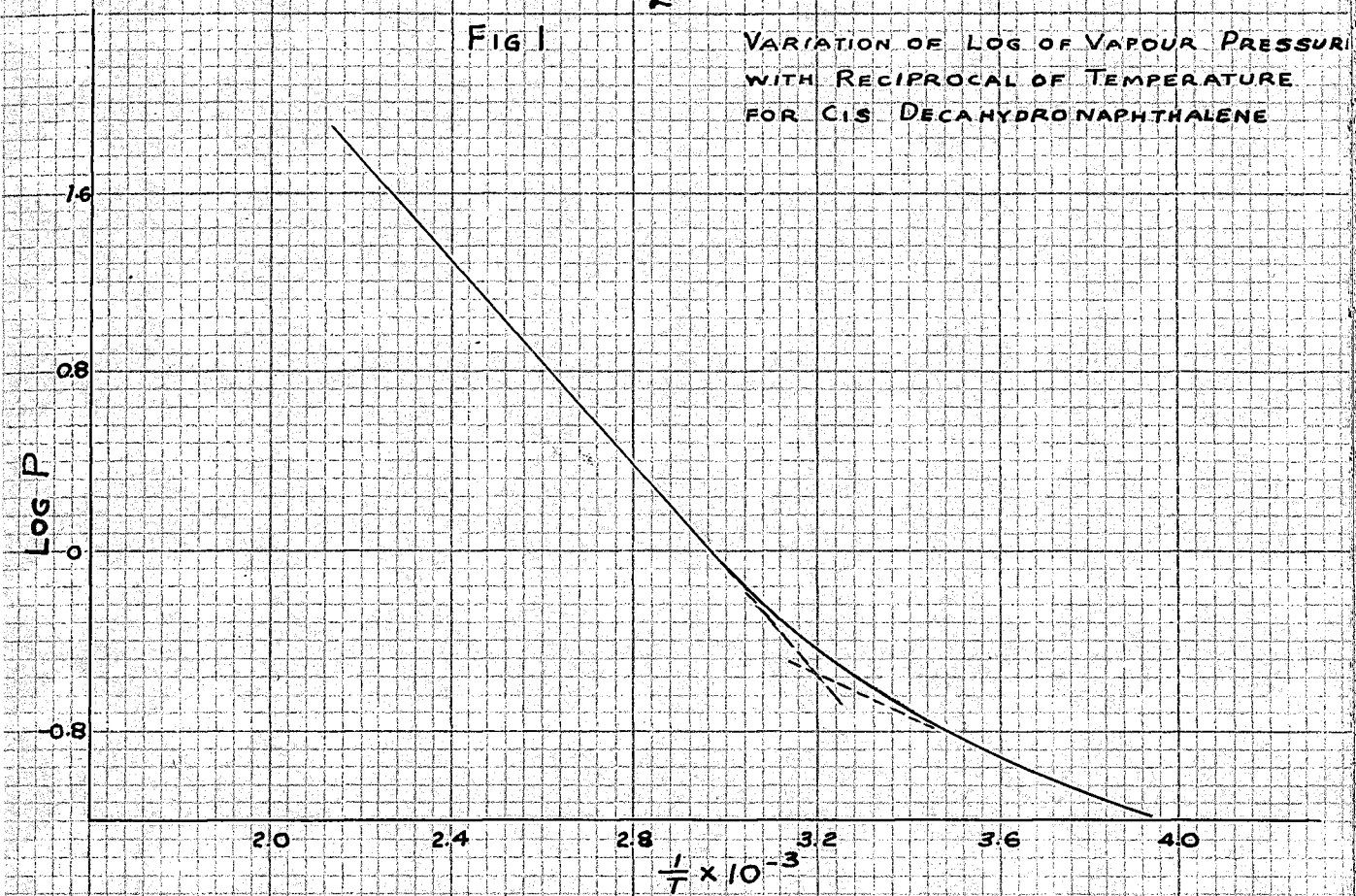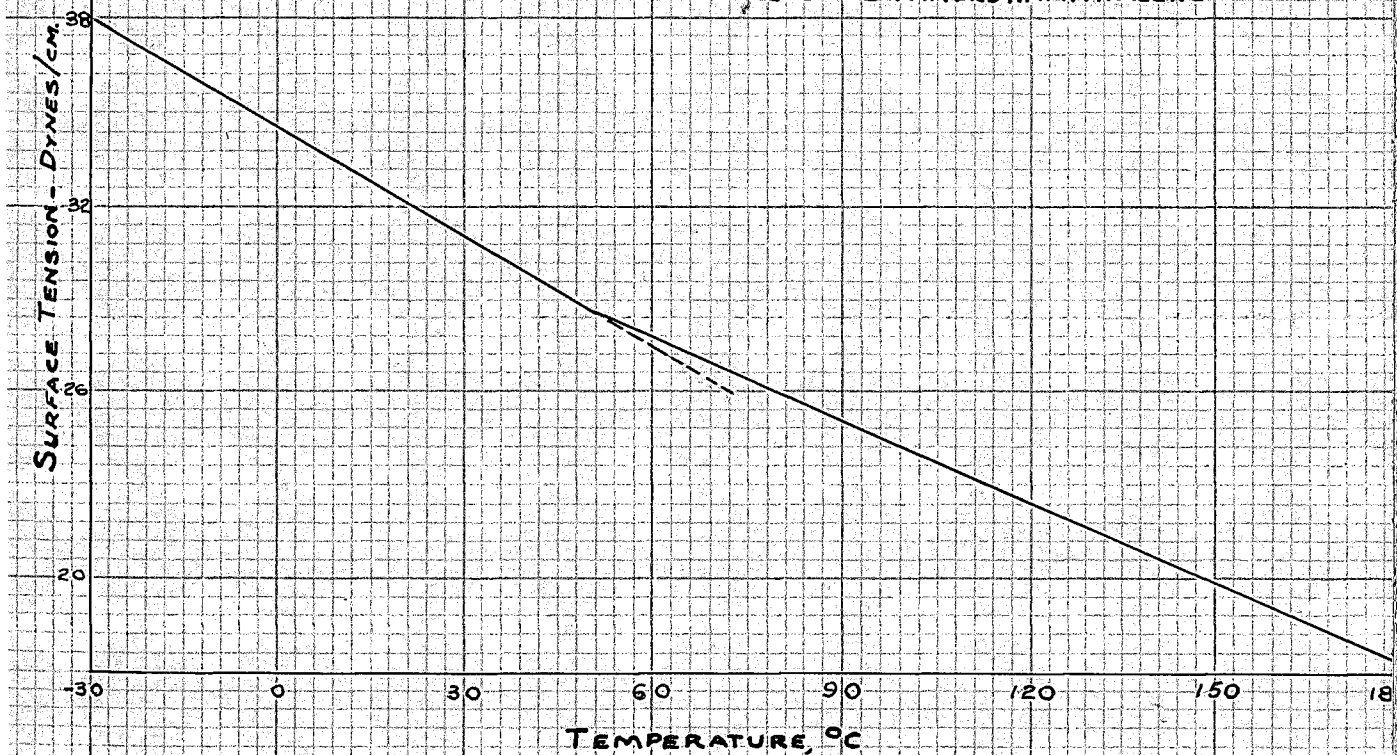
Fig. 3

VARIATION OF VERDET CONSTANT
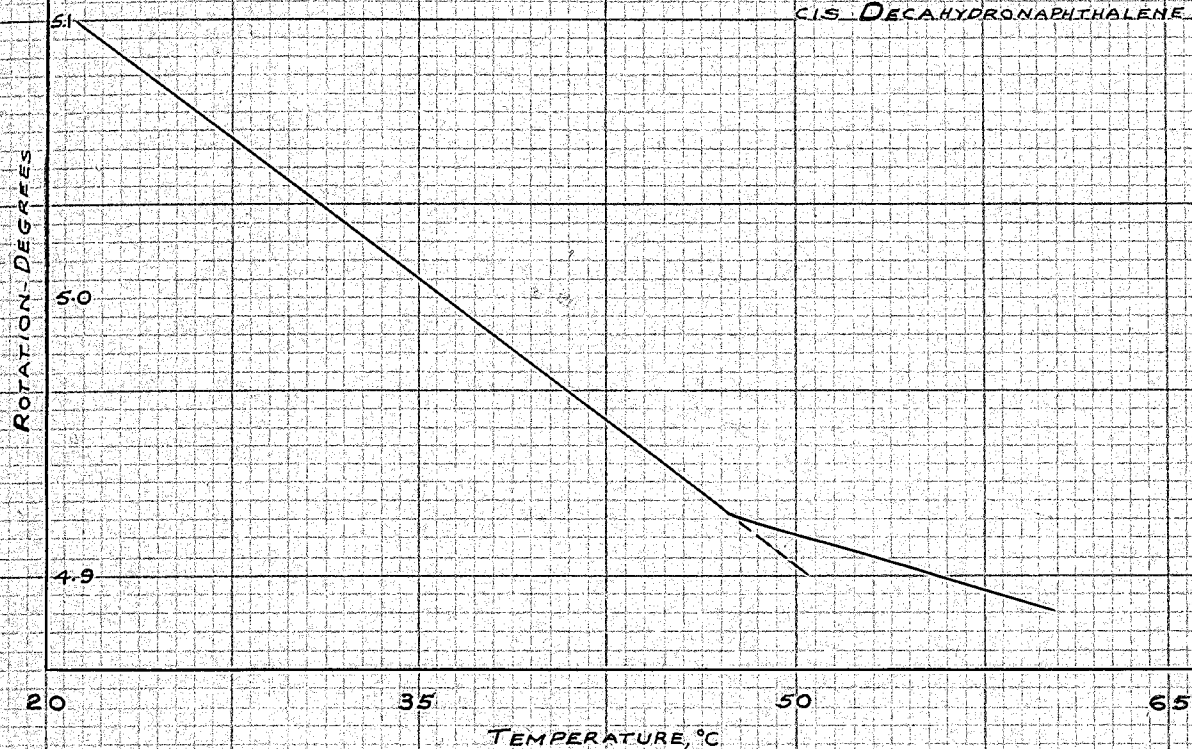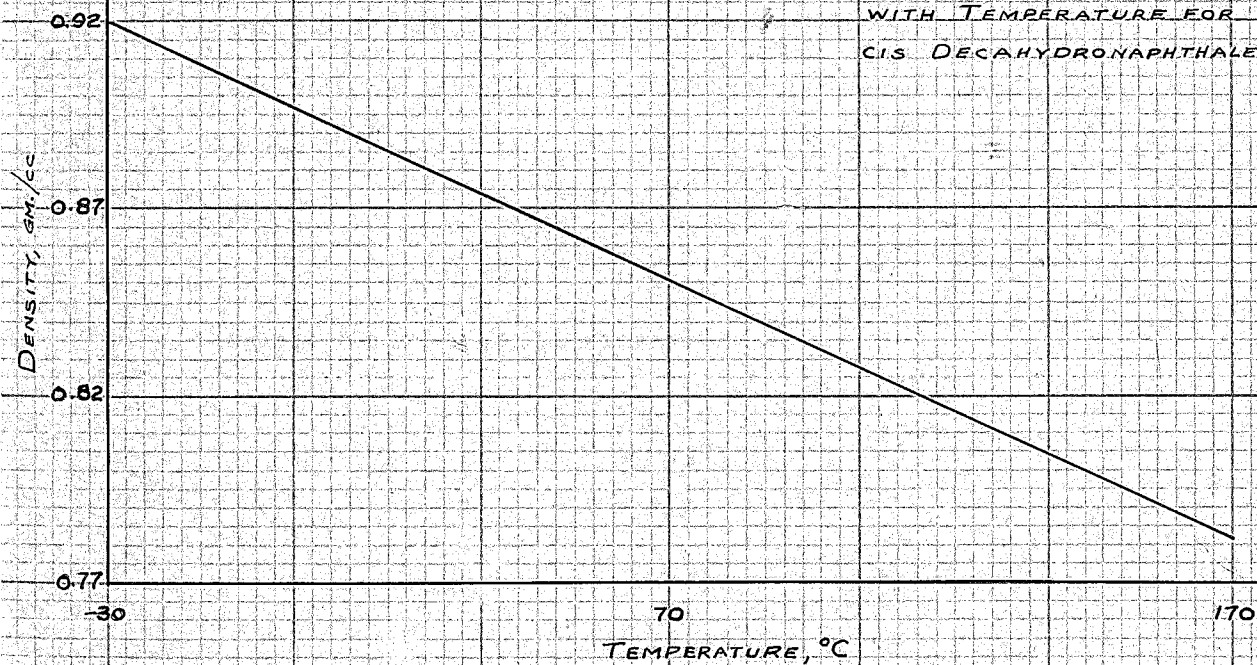WITH TEMPERATURE FOR
CIS DECAHYDRONAPHTHALENE

Fig 4

VARIATION OF DENSITY
WITH TEMPERATURE FOR
CIS DECAHYDRONAPHTHALENE

Phase Transitions

In a first-order phase transition at constant temperature and pressure there is, accompanying the transformation, a jump in entropy associated with the latent heat and a jump in the specific volume. The thermodynamic potential or Gibb's function, g, is the same for the two phases, but the first-order derivatives of the Gibb's function change discontinuously. In mathematical terms,

$$\left(\frac{\partial g}{\partial T}\right)_P = S$$

$$\left(\frac{\partial g}{\partial P}\right)_T = v$$

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_p}{T}$$

Thus, if for an ordinary transformation, the Gibb's function entropy, specific heat and volume are plotted as a function of the temperature with p constant, the results are as shown in (figure 5). If in a PT diagram (figure 6) AB is a line along which a transformation of the first-order takes place, then for the first-order transition,

$$g_2 - g_1 = 0$$

$$\left(\frac{\partial g_1}{\partial T}\right)_P - \left(\frac{\partial g_2}{\partial T}\right)_P = S_2 - S_1 = \frac{q}{T}$$

where q is the heat of transformation

and

$$\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T = v_2 - v_1$$
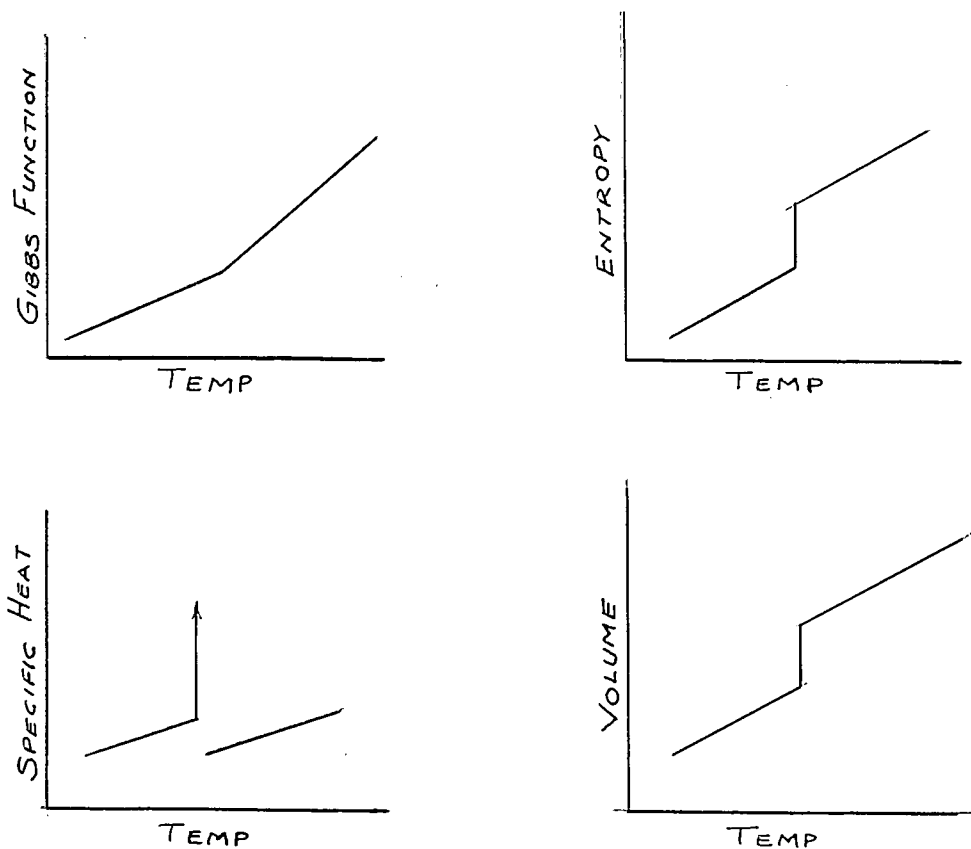
FIRST ORDER PHASE TRANSITIONS

Fig. 5
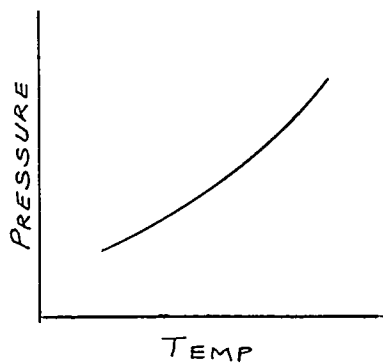
Fig. 6

Let x be a quantity which does not change in passing from one side to the other of AB in (figure 6) and let Δ p and Δ t be corresponding changes in p and T in passing along this curve. Then

$$\frac{\Delta p}{\Delta T} = \frac{\left(\frac{\partial x_2}{\partial T}\right)_P - \left(\frac{\partial x_1}{\partial T}\right)_P}{\left(\frac{\partial x_1}{\partial P}\right)_T - \left(\frac{\partial x_2}{\partial P}\right)_T}$$

Let x = g and we then obtain the Clausius-Clapeyron Equation

$$\frac{dp}{dt} = \frac{L}{T(v_1 - v_2)}$$

In a second-order phase transition, on the other hand, there is no change in entropy or volume at the transition point. The first-order derivative of the Gibb's function changes continuously as the substance passes from one phase to the other (figure 7). As can be seen, there is no step in the curve but a discontinuity in slope at the transformation point. Similarly the thermal measurements show no latent heat but a sharp discontinuity in specific heat (figure 8).

The following processes are generally regarded by physicists as second-order phase transitions:

      1: A ferro-magnetic metal such as iron and nickel becomes paramagnetic at the Curie point.

      2: A super-conducting metal becomes an ordinary conductor at a definite transition point. [6]

SECOND ORDER PHASE TRANSITIONS
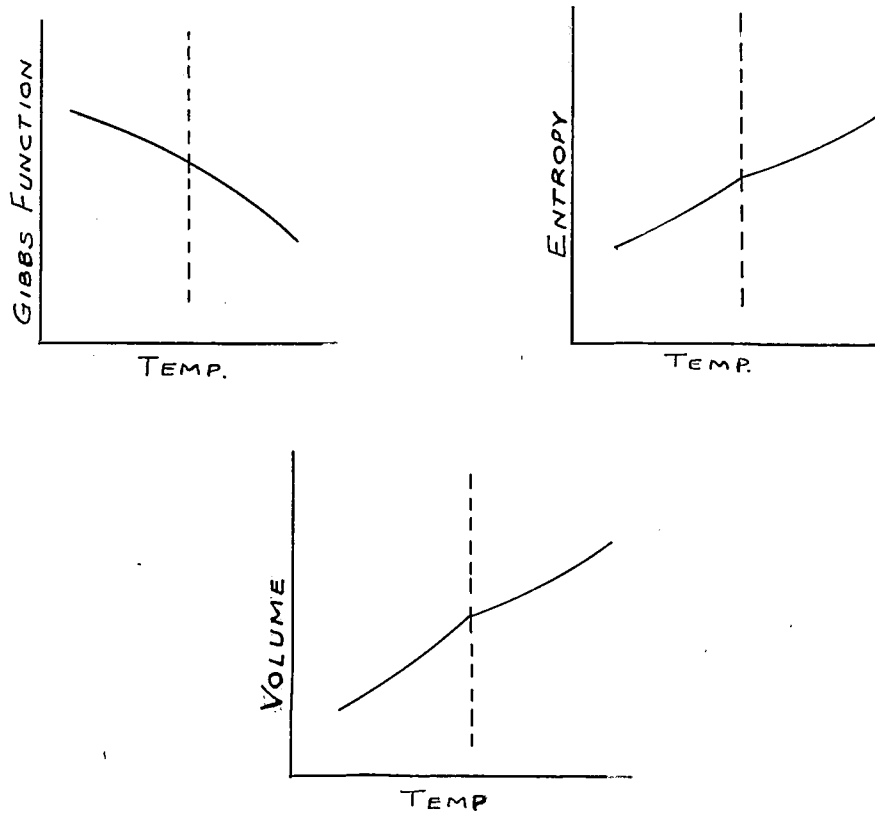
FIG. 7
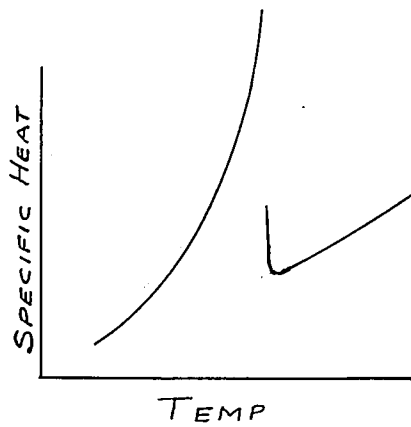
FIG. 8

3: The ammonium chloride effect. [1,2] The specific
heat of NH Cl as compared with NaCl is shown in (figure 9).
The sharp maximum at 243° K. represents the critical temperature
of a co-operative adsorption of energy which commences at much
lower temperatures and is not accompanied by a change in crystal
structure. It has been shown that in this and similar cases the
anomalous specific heat is due to a transition from a state in
which the molecules merely librate (wobble) about fixed orientations
to a state in which they are practically in free rotation. This is
again a co-operative phenomena, since a particular molecule be-
comes more free to rotate when its neighbors are already in rotation
for then the field produced by them approaches more closely to spher-
ical symmetry and the tendency to orientation is reduced.

4: The anomoly observed in the heat capacity of
potassium dihydrogen phosphate at the Curie temperature [16]. This is
shown in (figure 10). From the experimental entropy value for
this change and from studies of KH_2AsO_4 and $NH_4H_2PO_4$, Stephenson
and Hooley conclude that the hydrogen bonds in these crystals are
responsible for the transition.

5: Liquid He2 becomes Liquid Hel at various temp-
eratures and pressures, for example, the λ point where T = 2.19°K
and P = 38.65 mm. At this point the density of Hel is the same as
He2. In plotting the density curve vs. temperature (figure 11),
there is seen to be a discontinuity but no step at the λ point.
Similarly the thermal measurements show no latent heat but a sharp
discontinuity in the specific heat curve, (figure 12).

Fig. 9

SPECIFIC HEAT OF AMMONIUM CHLORIDE

COMPARED TO SODIUM CHLORIDE

NH4Cl

NaCl

Sp. Heat - Cal./Mole/Deg.

Temperature, °K
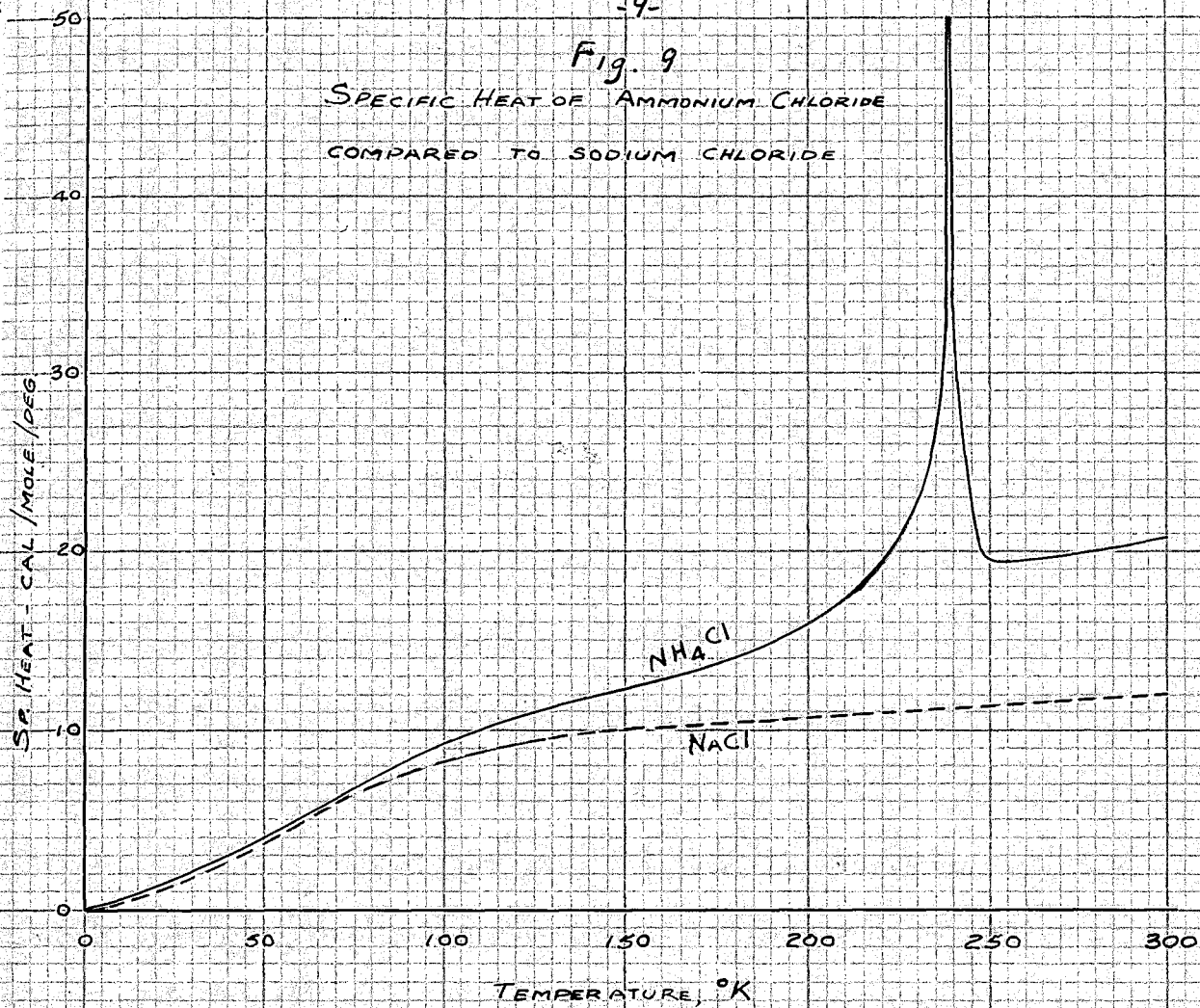
Fig 10.

SPECIFIC HEAT OF KH_2PO_4

Sp. Heat, Cal./Mole/Deg.

Temperature, °K

Fig. 11
Density of He

Fig. 12
Specific Heat of He
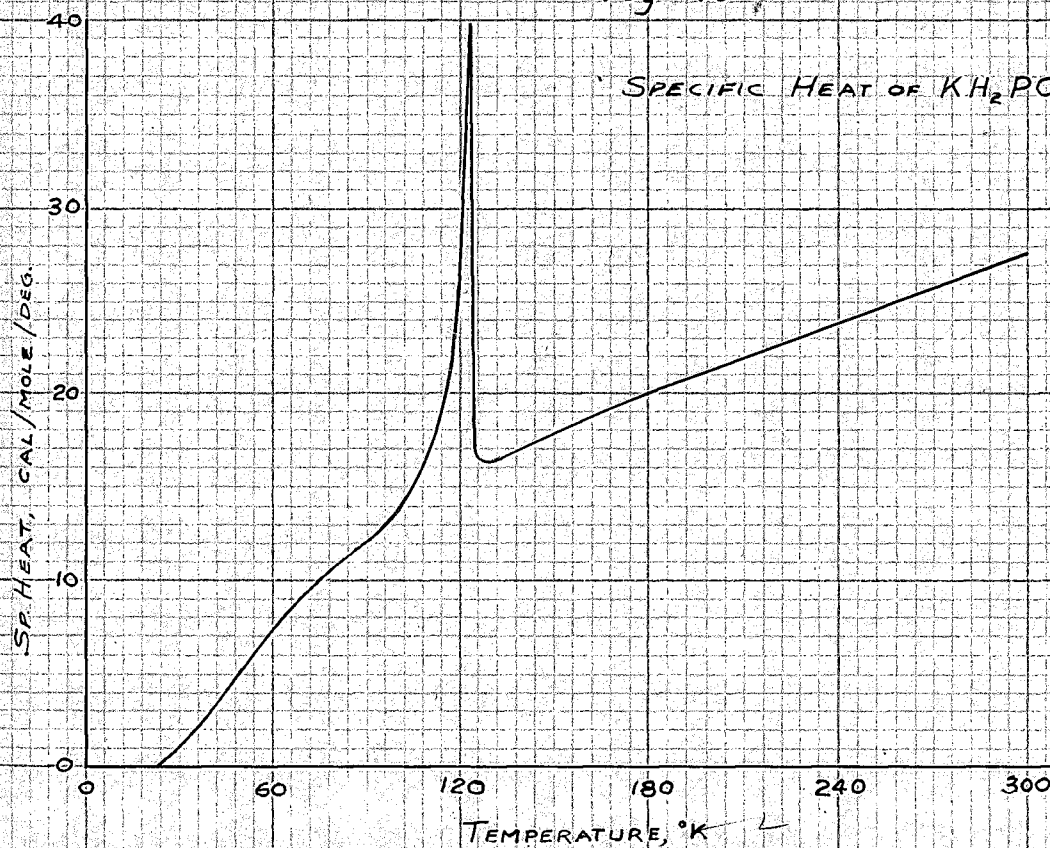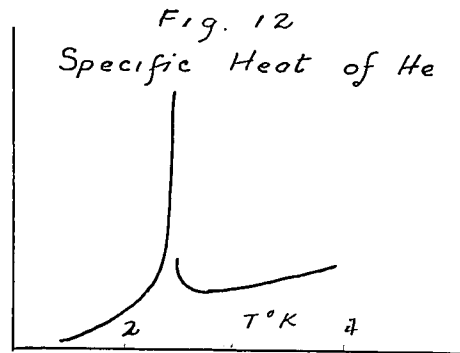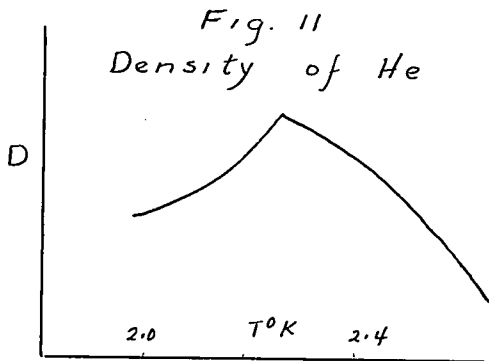
For a transformation of the second-order,

$$g_2 - g_1 = 0$$

$$\left(\frac{\partial g_1}{\partial T}\right)_P - \left(\frac{\partial g_2}{\partial T}\right)_P = 0$$

$$\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T = 0$$

But in all these processes the quantities, specific heat and density show discontinous changes during the phase transition.

Since

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(-\left(\frac{\partial g}{\partial T}\right)_P\right)_P = -\frac{\partial^2 g}{\partial T^2}$$

$$-\left(\frac{\partial v}{\partial P}\right)_T = -\frac{\partial}{\partial P}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_T = -\frac{\partial^2 g}{\partial P^2}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_P = \frac{\partial^2 g}{\partial T \partial P}$$

it follows that a second-order transition is characterized by changes in the second-order derivatives of the Gibb's Function.

Also

$$\left(\frac{\partial^2 g_1}{\partial T^2}\right)_P - \left(\frac{\partial^2 g_2}{\partial T^2}\right)_P = \frac{C_{P_2} - C_{P_1}}{T}$$

$$\left(\frac{\partial^2 g_2}{\partial P^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial P^2}\right)_T = \left(\frac{\partial v_2}{\partial P}\right)_T - \left(\frac{\partial v_1}{\partial P}\right)_T$$

$$\left(\frac{\partial^2 g_2}{\partial T \partial P}\right) - \left(\frac{\partial^2 g_1}{\partial T \partial P}\right) = \left(\frac{\partial v_2}{\partial T}\right)_P - \left(\frac{\partial v_1}{\partial T}\right)_P$$

If then x is a quantity which does not change in passing from one form to the other and let Δ p and Δ t be the corresponding changes in p and t in passing along the curve dividing the two states then:

$$\frac{\Delta p}{\Delta T} = \frac{\left(\frac{\partial x_2}{\partial T}\right)_P - \left(\frac{\partial x_1}{\partial T}\right)_P}{\left(\frac{\partial x_1}{\partial P}\right)_T - \left(\frac{\partial x_2}{\partial P}\right)_T}$$

Let x = s and x = v

$$\frac{\Delta p}{\Delta T} = \frac{\left(\frac{\partial S_2}{\partial T}\right)_P - \left(\frac{\partial S_1}{\partial T}\right)_P}{\left(\frac{\partial S_1}{\partial P}\right)_T - \left(\frac{\partial S_2}{\partial P}\right)_T} = \frac{C_{P_2} - C_{P_1}}{T\left\{\left(\frac{\partial v_2}{\partial T}\right)_P - \left(\frac{\partial v_1}{\partial T}\right)_P\right\}}$$

and

$$\frac{\Delta P}{\Delta T} = \frac{\left(\frac{\partial v_2}{\partial T}\right)_P - \left(\frac{\partial v_1}{\partial T}\right)_P}{\left(\frac{\partial v_1}{\partial P}\right)_T - \left(\frac{\partial v_2}{\partial P}\right)_T}$$

From these two equations:

$$C_{P_2} - C_{P_1} = \frac{T\left\{\left(\frac{\partial v_2}{\partial T}\right)_P - \left(\frac{\partial v_1}{\partial T}\right)_P\right\}^2}{\left(\frac{\partial v_1}{\partial P}\right)_T - \left(\frac{\partial v_2}{\partial T}\right)_T}$$

These are the assumptions on which Ehrenfest and Von Laue have based their work. Epstein suggests the assumption goes too far when they differentiate the equation $g_2 - g_1 = 0$, this implying that contact exists along the whole line (or a finite part of it) of the intersection of the surfaces g_2 and g_1. There is nothing in the experimental observations to justify this assumption. Theoretically it is also a remote case. It is a far more common occurence that the two surfaces are in contact in a singular point, that is, the equation $g_2 - g_1 = 0$ is satisfied in just one point, whose co-ordinates we will denote as p_0, T_0. We now wish to find what takes place at $p_0 + dp$, $T_0 + dT$ and it is seen that transformations are possible if not in the point $p_0 T_0$ itself, in its immediate vicinity as is illustrated in the (p,T) diagram of (figure 13).

fig. 13
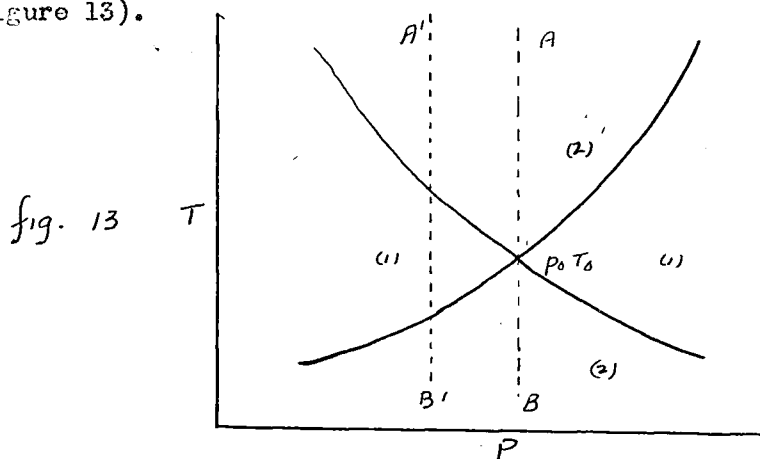
There are two lines in which the phases (1) and (2) can co-exist and they intersect at a singular point $p_0 T_0$. When the substance is cooled at a pressure exactly coinciding with that of the intersection (dotted line AB), no transformation takes place. If it is cooled at a slightly different pressure A'B' it is transformed first from phase

(2) into phase (1) and at a lower temperature back into (2) again.
Some of the experimentally measured anomalies present features com-
patible with this picture: as the temperature is changed the specific
heat jumps discontinuously and, at a slightly lower temperature
jumps back to the initial value.

Since no discontinuity was found in the density
curve of cis decahydronaphthalene, any transition which takes place
must necessarily be a second-order phase transition.

We have shown that:

$$\frac{C_p}{T} - \left(\frac{\partial S}{\partial T}\right)_P = -\frac{\partial^2 g}{\partial T^2}$$

that is the specific heat curve is a first-order derivative of the
entropy curve. Since, in a second-order transition, the slope of the
entropy curve changes at the transition point, the specific heat
curve should be discontinuous at the transition point. It is this dis-
continuity we are endeavoring to detect.

If we could possibly obtain a heating rate low
enough to bring about transition without raising the temperature and
without other effects taking place the specific heat curve would

appear as follows:

c_p
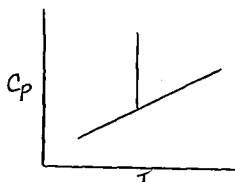
That is we would get some readings with no temperature rise at all

or infinite specific heat. Practically the curve would be of the

form:

c_p
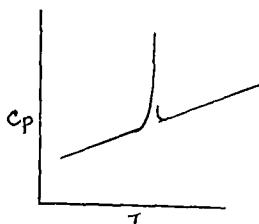
When the heat of transition is very small compared to the specific

heat, the curve would have the form:

c_p
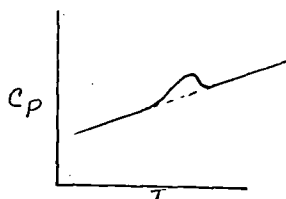
It is this latter form of specific heat curve which is expected for

cis deccahydronaphthalene.

The Adiabatic Method and Errors Involved:

The adiabatic method is considered the most accurate

for long experiments as were carried out here in the first part of the

work. By reducing the value of the thermal leakage to a minimum this

method reduces errors in its measurements and inconstancies in its values

due to convection, evaporation, radiation, solid conduction and evapor-

ation. By this, lags are made nearly constant over the whole experimental

period and errors due to lags are reduced accordingly.

Experimental calibration eliminates the systematic errors of the calorimeter. The variation in these effects therefore, are really the errors. It has been calculated that the heat required for the evaporation to maintain saturation is below 0.1% of the specific heat, so any variations in this amount would be negligible.

The stirring motor has a constant rate of 75 r.p.m. which produces a temperature rise of not more than $0.0005^{\circ}C$ per min. at a temperature of $50^{\circ}C$. This is equivalent to an energy input of 0.003 watts. Applying a correction for this amount in the calculations again gives the desired accuracy.

The accuracy of measurement of energy input was shown to be 0.28% as can be shown below. The current input of 0.12 amps and the voltage from the volt box of 0.195 volts can be measured to 0.00001 volts giving 0.008% and 0.005% precision respectively. Time intervals of 6000 seconds accurate to one second and temperature intervals of 2° accurate to 0.0005° giving 0.02% and 0.25% precisions respectively. This insures an accuracy of 0.28% energy input.

It will be seen that temperature measurements involve the greatest error as the temperature intervals are reduced to obtain greater sensitivity.

The Isothermal Method:

While the adiabatic method has been proven the best for protracted experiments, it is not always the most accurate method if the experiment can be conducted as short runs. The apparatus was rearranged therefore so that the isothermal method could be used.

Since the heating rate is proportional to the

thermal head we have

$$V = K \, \varphi$$

where V = Rate of temperature change in calorimeter

K = Thermal leakage modulus

φ = Thermal head

The temperature loss formula is, therefore,

$$\eta = VT = K \, T \, \varphi$$

In the adiabatic method since φ is zero, errors

caused by temperature loss are consequently reduced to a minimum.

But if φ can be accurately determined, the error in determining the

temperature loss is caused then only in K failing to remain constant.

After each experimental period, in a calibration period the rate

of cooling was redetermined. Consequently these errors are reduced to

an order compatible with the adiabatic method when the same heating rate

was used.

Apparatus:

The apparatus used in this investigation is the

same as that used by Mead[7] and McLellan[8] and is adequately described

in their theses. A brief resume will be given here and any changes

particularly noted.

The Calorimeter is the same as used by previous

workers and was constructed similarly to Williams and Daniels.[13]

It consisted of a thin-walled spun copper cup holding the cis

decahydronaphthalene , this cup being set in a large cylindrical copper container, 8 cm in diameter and 12 cm high. To the bottom of the container, 650 gms of lead were soldered to lessen the buoyancy pressure on the stirring shaft during operation. The inside cup was fitted with a grooved fibre ring, a copper sluve running from the groove to the lid. The lid contains openings for necessary heating and measuring equipment, viz, thermopile, heating coil leads and shaft for the stirrer. Attached to the lid with rubber cement was a thin washer of neoprene rubber. The other side of the washer was coated with rubber cement and the lid immediately screwed tightly in place.

Bath Medium:

The bath is stirred by two high speed shafts, each equipped with several three bladed propellors.

It has been found in previous work that the use of glycerine for a bath medium below temperatures of approximately 40°C involved too large temperature gradients in the bath. Difficulty due to its leakage into the calorimeter and its high vapour pressure was experienced using water. From vapour pressure vs. viscosity curves, a 95% aqueous glycerol solution was considered satisfactory. Adding 5% water to the glycerine lowers the viscosity at 25°C from 945 centipoises to 366 centipoises. Temperature gradients in the bath for this viscosity and at 25°C did not exceed 0.01°C. This was considered satisfactory.

The vapour pressure at this temperature and concentration was 2.4 mm. and no difficulties were experienced with this vapour pressure.

Bath Heating Circuit:

The electrolytic bath heating circuit was modified to give better temperature control. An adjustable transformer (Variac Type 100 Q) was installed in place of several variable resistances. An ammeter was also placed in the circuit. A current of 0.65 amp. was required at 50° C in the adiabatic method when the cup was heated with an input of 0.1 watts. A current of 0.45 amps was required to keep the bath temperature constant at 50°C.

The outer bath heater was used only to bring the bath up to the temperature of the experiment and then only the electrolytic heater was used.

Use of the photoelectric cell and relay for controlling bath temperatures was also discontinued as better control was obtained with manual operation of the transformer.

Thermocouple:

A new thermopile was constructed of #36 B and S gauge copper wire and #30 B and S copel wire, five couples being used in each junction. The wires were twisted together four times, soldered and each junction insulated with glyptal varnish. The thermopile was calibrated using two baths, 10°C apart in temperature. The temperatures of the baths were measured with two platinum resistance thermometers.

The results given below are plotted in (figure 14)

Table I   Temperature Dif. ^{o}C.   E.M.F. μvC.

62-52	208.0
55-45	206.0
52-42	205.0
32-22	201.5

With all junctions at the same temperature, the e.m.f. set up was $1\mu v$ corresponding to 0.005^{o}C. This small temperature difference may have been due to irregularities in the bath and the temperature was considered constant.

Cup Heater Circuit:

The electrical energy was supplied from 120 amperehour lead storage battery, the quantity being controlled by a rheostat of nichrome wire in the battery circuit. The voltage drop across the heater was measured by a Type K Universal Potentiometer, first being reduced to a measurable quantity through a volt-box. The current is calculated from the voltage drop across a one ohm standard resistance. From the e.m.f. indicated by the potentiometer the voltage drop across the leads and across the standard resistance must be subtracted to give the voltage drop across the heater itself. The resistance of the leads was measured. Results were as follows:

24°C - 0.1795 ohms.

50°C - 0.1828 ohms.

The resistance varies linearly with temperature between these points.

Fig. 14

Calibration of Thermopile
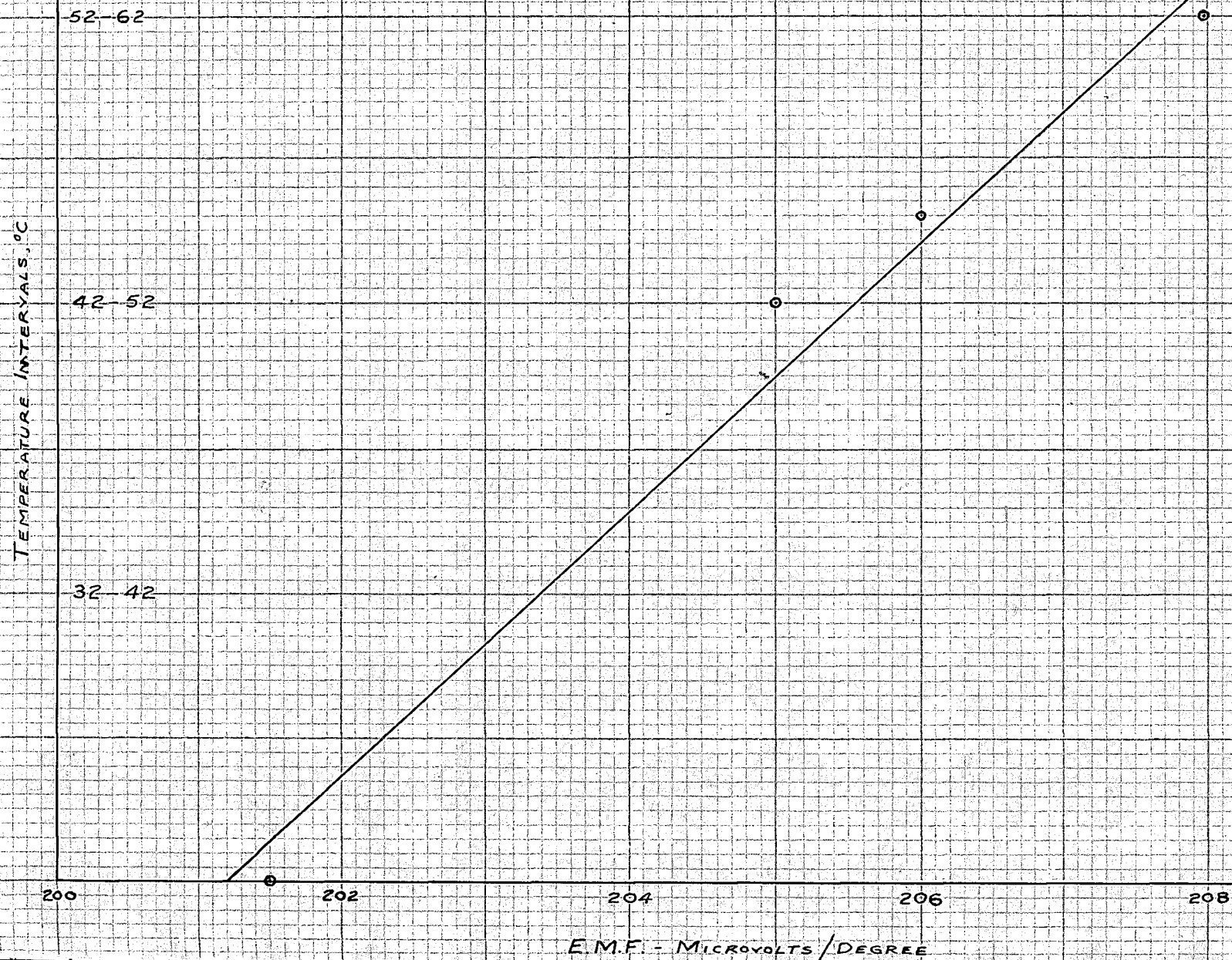
Calibration:

The calorimeter had been previously calibrated with toluene[8]. The water equivalent was found to be 38.0 joules + 0.1 joules/10°C.

Operation:

Specific Heat Determinations

Adiabatic Method:

The sample (150g - 160g) was placed in the cup, the calorimeter assembled and placed in the bath. All leads were connected and the battery current passed through the dummy heater. The bath and cup were both raised to 40°C and their temperatures equalized. When steady conditions were maintained, the current was switched to the cup heater and readings of time and temperature taken at regular intervals. Checks were made as often as possible on voltage and current input. A heating rate of 0.1 watts was used.

Isothermal Method:

The apparatus was assembled as for the adiabatic method. A two-way switch was inserted in the thermopile galvanometer circuit, the other half of the switch being connected to the e.m.f. terminals of the potentiometer. The galvanometer scale was calibrated for various temperature differences as measured by the potentiometer. It was found a temperature difference of 0.2°C (40.1 μv from the thermopile at 50°C) deflected the scale 24.5 cm. This value was checked periodically throughout the runs varying not more than 0.5 cm.

The leads from the thermopile were disconnected from the potentiometer and the leads from the cup-heater circuit were re-connected. The bath and calorimeter were brought to the desired temperature using the cup-heater, electrolytic bath heater and outer heater. While current was flowing through the cup-heater several determinations of voltage and current were made. The current was switched to the dummy heater when not in use. After steady conditions had been maintained for a short period, the cup heater and stopwatch were switched on simultaneously. A current reading was taken and the cup-heater switched off after 45 seconds. To ensure complete equilibrium of the liquid, before each determination the calorimeter was held constant at the initial temperature for an hour. The approximate temperature rise used in first and second runs were $0.2^{\circ}C$ and $0.02^{\circ}C$ respectively.

Operation (Continued):

Cooling Curves:

Apparatus is assembled as for a specific heat run with the exception of connecting the thermopile leads to the potentiometer instead of to the galvanometer. Since no measurements of power input to the cup are needed, these leads may be disconnected from the potentiometer and the heating coil used only for obtaining the desired temperatures.

Then one adjusts the cup and bath temperatures using the heating coil in the cup and the electolytic bath heater for the bath. The decalin should be approximately $53^{\circ}C$ and the bath $50^{\circ}C$. When the desired bath temperature is reached, it is kept constant by

adjusting the heat input to the electrolytic bath heater to a low value. During the cooling, simultaneous readings of time and thermocouple e.m.f. are taken at 2-3 minutes intervals, one junctions of the thermopile being in the bath and the other in the decalin. The e.m.f. is determined to the nearest μv, i.e. 0.005°C, so is of the same order of accuracy as the platinum resistance thermometer. Readings are continued until the decalin has approached within 0.1° of the bath temperature.

Heating Curves:

The procedure for obtaining the heating curves is almost exactly the same as for the cooling curve but the bath is now at a temperature greater than 50°C and the decalin below 50°C. To avoid hysteresis effects, it was avoided using the heating coil to bring it to a temperature where readings could be started but to do this by heat transfer from the bath. In this way, no part of the decolin will have been heated above 50°C before readings are commenced.

It should be noted that heat input to the bath equals heat lost to surroundings plus heat lost to decalin whereas for the cooling curve, heat input equals heat lost to the surroundings minus heat gained from the decalin.

Calculations:

For the adiabatic runs the method of calculation of specific heat values was the same as that used by McLellan.[8]

For the isothermal runs the temperature rise must be calculated before the specific heat can be determined.

A sample set of readings is given in Table II :

Table II

Resistance (R)	Current (Amp.)	Time (Sec.)	Scale Reading
3.0537	0.49343	92	16
		126	20
		139	21
		156	22
		189	23
		250	24
		351	24
		436	23
		536	22
		645	21
		778	20
		876	19
		1011	18
		1135	17
		1290	16

The scale readings were converted to temperatures, a graph of temperature vs time was plotted (figure 15).

By interpolation back to zero time the true rise in temperature was found. This method was not very accurate, however, and the following calculations were used, as given by White.[5]

Fig 15

Isothermal Heating and Cooling Curve

Y-axis: ΔT - °C

X-axis: Time - Sec

-25-

We have:

$\Delta\theta$ = the temperature rise due to heat that stays in the calorimeter.

η = the temperature loss due to heat lost.

Therefore: $\Delta\theta + \eta = \Delta\theta'$ the temperature change corresponding to the total measured quantity of heat.

Assume the cooling of the calorimeter, that is, all change not due directly to the measured heat, has the formula:

$$\eta = \omega + K\varphi$$

ω = heat of stirring

K = thermal leakiness

φ = thermal heat

The observed rate of cooling is given in the formula :

$$V_\lambda - \omega = K\varphi$$

The proportional part of this rate for the experimental period is:

$$\frac{(V_\lambda - \omega)\varphi_x}{\varphi_\lambda}$$

φ_x = average thermal head in experimental period.

φ_λ = average thermal head in calibration period.

Therefore the total rate of cooling for the experimental period is:

$$= \omega + (V_\lambda - \omega)\frac{\varphi_x}{\varphi_\lambda}$$

Formula for temperature loss:

$$\eta = \left[\omega + (V_\lambda - \omega)\frac{\varphi_x}{\varphi_\lambda}\right]T_x$$

But since φ_x is approximately equal to φ_λ it is advantageous to substitute

$$1 + \frac{\varphi_x - \varphi_\lambda}{\varphi_\lambda} \qquad for \qquad \frac{\varphi_x}{\varphi_\lambda}$$

$$\left[V_\lambda + (V_\lambda - \omega) \frac{\varphi_x - \varphi_\lambda}{\varphi_\lambda} \right] T_x = \eta$$

and with this quantity we obtain the true temperature rise using

$\Delta\theta + \eta = \Delta\theta'$. When the true temperature rise has been determined the specific heat is calculated as for the adiabatic method.

Discussion of Results:

Heating and Cooling Curves:

The heating and cooling curves were obtained to see if a change of slope could be noted in the region of transition. The results are necessarily qualitative because of insufficient knowledge of the thermal leakage modulus of the calorimeter. This quantity must be known accurately to determine specific heats.

The time-thermocouple e.m.f. measurements from which were calculated temperature differences are given in tables 3,4,5. The logarithm of the temperature difference is plotted vs time. As can be seen figures 16, 17 b, show definite breaks in the region varying between 50.29°C - 50.4°C. Figure 17 a, shows no break. This was possibly due to contamination of the decolin through leakage of the calorimeter or perhaps the more rapid rate of heating and cooling has mashed the effect of the transition.

The plotting of $\log \Delta t$ vs time is based on Newton's Law of Cooling.

Over a short interval of time $d\theta$ a quantity of heat passes through the walls of the calorimeter from the bath.

According to Newtons Law of cooling

$$\frac{dQ}{d\theta} = K(t_b - t)$$

where

t_b = bath temperature

t = decahydronaphthalene temperature

K = constant

All the heat is used in raising the temperature of the calorimeter and its contents.

Therefore: $dQ = \omega C_p\, dt + W\, dt$

Where

ω = water equivalent of the decalin

C_p = specific heat of the decalin

W = water equivalent of the calorimeter

dt = rise in temperature

Combining these two equations we obtain:

$$\omega C_p\, dt + W\, dt = K(t_b - t)\, d\theta$$

$$K\, d\theta = \frac{(\omega C_p + W)\, dt}{(t_b - t)}$$

$$\int_0^\theta K\, d\theta = \int_{t_1}^t \frac{t(\omega C_p + W)\, dt}{t_b - t}$$

Over a temperature range of only a few degrees C_p and W may be considered constant.

Therefore:
$$K\theta = -\left[(\omega C_p + W)\ln(t_b - t) \right]_{t_1}^t$$

$$= (\omega C_p + W)\ln\left(\frac{t_b - t_1}{t_b - t}\right)$$

Therefore: $K_1 0 = \ln(t_b - t)$

Similarly for a cooling curve:

$$K_2\theta = \ln(t - t_b)$$

A normal logarithmic cooling curve should be a straight line. Any irregularities in cooling would show by a change in the slope of the line.

Table III

Heating and Cooling Curves - Run #1.

Weight of sample - 151.809 g.

Heating Curve		Cooling Curve	
Temperature of Bath - 50.86°C.		Temperature of Bath - 49.9 °C	
Transition Temperature = 50.39 °C		Transition Temperature = 50.29 °C	
Time (sec.)	Log T	Time (sec.)	Log T
0	0.6946	0	0.3927
321	0.6646	187	0.3434
678	0.5289	418	0.2923
960	0.4609	565	0.2695
1356	0.3617	733	0.2253
1788	0.2577	912	0.1818
2172	0.1673	1122	0.1367
2613	0.05311	1343	0.0864
3007	-0.0555	1626	0.0334
3458	-0.1662	1915	-0.0306
3812	-0.2291	2258	-0.1057
3979	-0.2696	2528	-0.1637
4110	-0.3098	2850	-0.2299
4245	-0.3565	3200	-0.3098
4440	-0.4089	3435	-0.3556
4616	-0.4559	3690	-0.4067
4832	-0.5376	3965	-0.4647
5004	-0.6108	4360	-0.5317

Table III (Continued)

Time (sec.)	Log T	Time (sec.)	Log T
5303	-0.7077	4900	-0.6108
5677	-0.8327	5436	-0.7077
6137	-1.0078	6074	-0.8327
6612	-1.3010	7456	-0.0088

FIG 16
HEATING AND COOLING CURVES
of
CIS DECAHYDRO·NAPHTHALENE
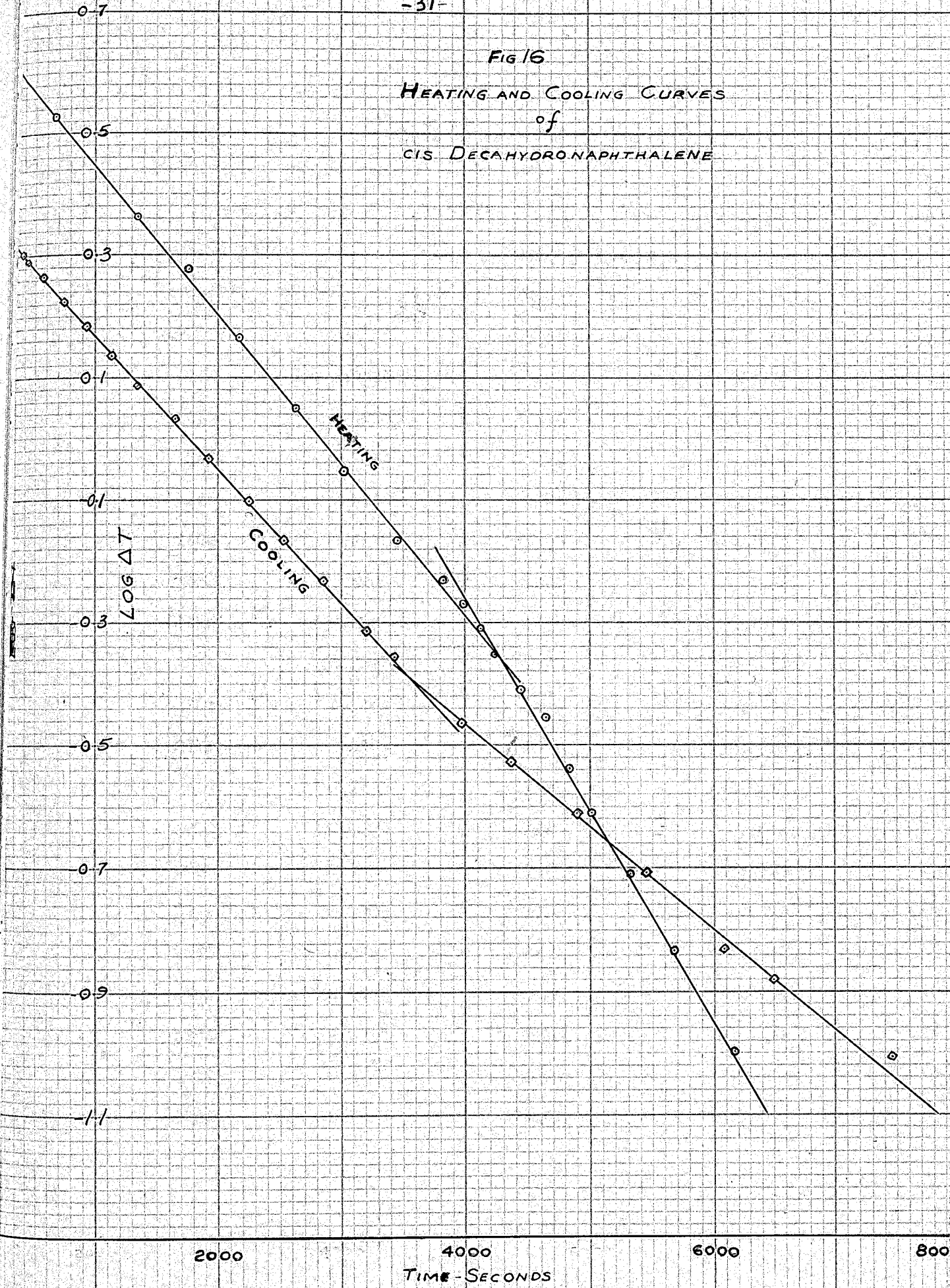
Table IV

Heating and Cooling Curves - Run #2.

Weight of sample = 151.280

Heating Curve		Cooling Curves	
Temperature of Bath = 51.63°C		Temperature of Bath = 48.765°C	
Time (sec.)	Log T	Time (sec.)	Log T
0	0.9025	0	0.7513
370	0.8041	354	0.6590
759	0.7033	766	0.5599
1148	0.6042	1053	0.4900
1380	0.5478	1143	0.4683
1610	0.4900	1243	0.4456
1818	0.4378	1350	0.4232
2024	0.3892	1438	0.3979
2208	0.3444	1555	0.3711
2420	0.2923	1678	0.3424
2617	0.2465	1802	0.3139
2830	0.1975	1930	0.2810
3005	0.1523	2077	0.2455
3211	0.1038	2230	0.2095
3430	0.0531	2407	0.1673
3680	-0.0088	2572	0.1206
3904	-0.0696	2790	0.1719
4177	-0.1331	3038	0.0118
4385	-0.1721	3322	-0.0540

Table IV (Continued)

Time (sec.)	Log T	Time (sec.)	Log T
4590	-0.2306	3640	-0.1337
4763	-0.2484	4054	-0.2299
4998	-0.3279	4680	-0.3904
5157	-0.3556	5350	-0.4920
5417	-0.4295		
5662	-0.4647		
5960	-0.5467		
6265	-0.6118		
6580	-0.7077		
7123	-0.8321		
7900	-0.0088		

Table V

Heating and Cooling Curves - Run #3

Weight of Sample - 151.280

Heating Curve		Cooling Curve	
Temperature of Bath = 50.86 °C		Temperature of Bath = 49.9°C	
Transition Temperature = 50.1 °C		Transition Temperature 50.4 °C	
Time (sec.)	Log T	Time (sec.)	Log T
0	0.6902	0	0.4456
197	0.6355	212	0.4065
462	0.5821	419	0.3617
670	0.5353	636	0.3139
1206	0.4150	896	0.2577
1375	0.3802	1160	0.2014
1581	0.3345	1452	0.1367
1915	0.2577	1685	0.0864
2262	0.1818	1947	0.0334
2516	0.1206	2137	-0.0088
2850	0.0531	2370	-0.0545
3036	0.0128	2608	-0.1051
3234	-0.0311	2870	-0.1637
3460	-0.0794	3173	-0.2306
3790	-0.1487	3364	-0.2692
4070	-0.2132	3735	-0.3316
4227	-0.2487	4020	-0.3798

Table V (Continued)

Time (sec.)	Log T	Time (Sec.)	Log T
4324	-0.2684	4131	-0.4067
4522	-0.3188	4390	-0.4647
4700	-0.3556	4793	-0.5327
4977	-0.4067	5200	-0.6108
5254	-0.4647	5700	-0.7077
5573	-0.5327	6383	-0.8177
5918	-0.6106		
6337	-0.7077		
6948	-0.8794		

Fig 17
Heating and Cooling Curves
of
cis Decahydronaphthalene
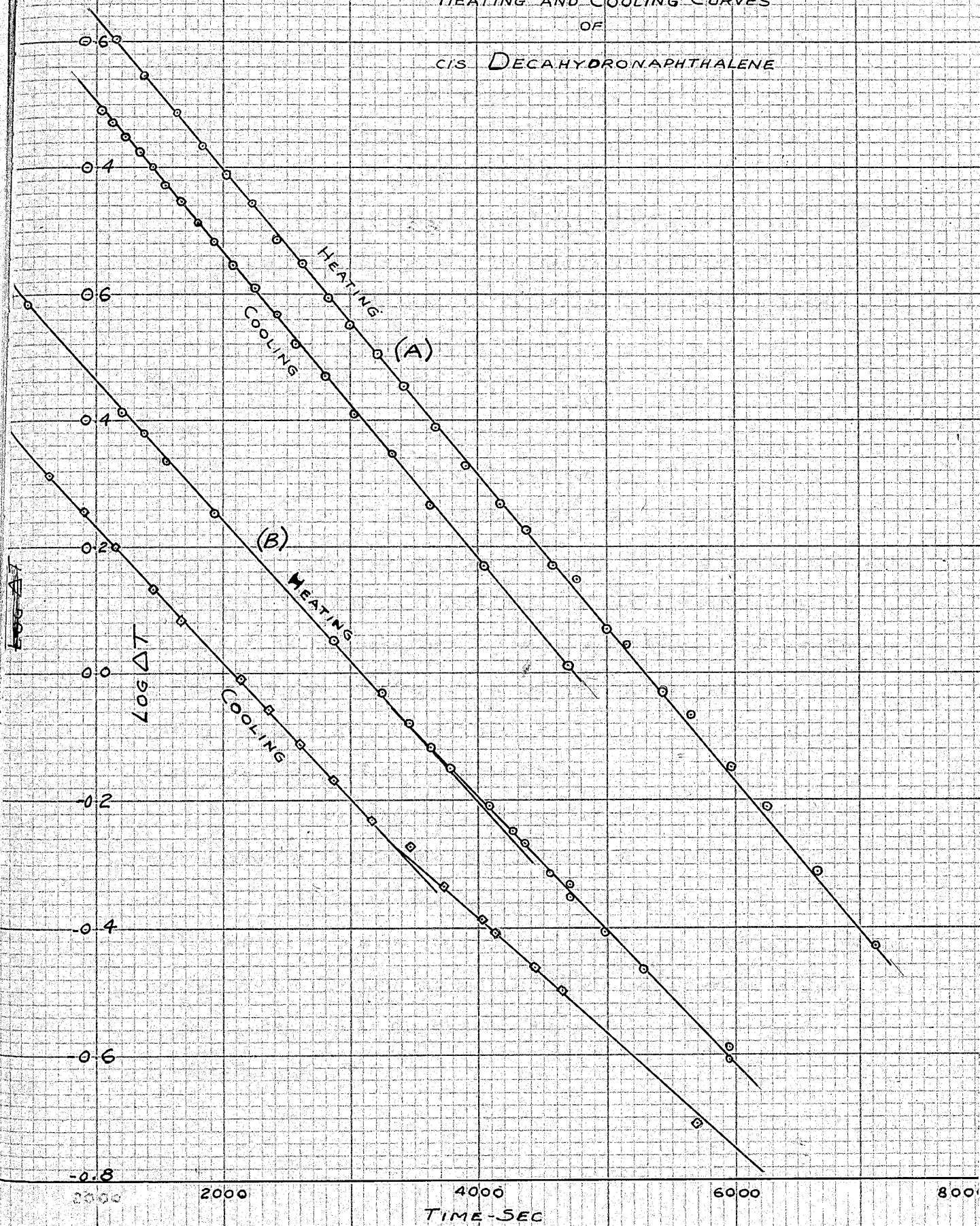
Specific Heat Curves:

It has been shown that the specific heat curve should be of the form given in (figure 8). The results obtained by the adiabatic method are given in table VI.

The curves (figure 8) have only a small change in slope at the transition point. The reasons for this may be as follows:

1. The heat of transition for cis decahydronaphthalene is small compared with the specific heat.

That is $(C_{p\alpha} - C_p) dt = dH$

where

$C_{p\alpha}$ = measured specific heat

C_p = real specific heat

dH = differential heat of transition

2. The transition requires a finite time and the ratio heat input being used in the transition to that used in raising the temperature is influenced by the heating rate, that is, it probalby requires a definite heat input for a definite time to effect the transaction so that a greater heat input would mean a greater proportion of heat being used to raise the temperature.

3. The higher the heating rate the higher the temperature gradient between the coil and the bulk of the liquid. This enables the transition to take place at a slightly lower bulk temperature òf the liquid. For a heating rate of 0.8 watts the temperature gradient between the heating coil and the decolin was calculated to be 0.3°C. At the heating rate of 0.1 watts used here this effect would be practically negligible.

Therefore it can be seen, the lower the heating rate, the more definite should be the change in the slope of the curve. At very low heating rates, however, the errors of the experiment, heat of stirring, temperature measurements, become appreciable.

The curve obtained in (figure 18 b) shows no discontinuity in the region of $50^{\circ}C$. This was due to impurities which had leaked into the decolin during the experiment.

The results from the isothermal runs are given in table 7. The curves, plotted in (figure 19) *show* a definite break at $50.2^{\circ}C$.
In obtaining (figure 19 b) a very low temperature rise was used, approximately $0.02^{\circ}C$. Since the limit of accuracy in controlling the temperature of the bath is $0.005^{\circ}C$, and the temperature rise per minute due to heat of stirring is $0.0005^{\circ}C$, then it can be seen errors will be appreciable. This accounts for the irregularities in the curve. Quantitatively the results are, therefore, unreliable but qualitatively they show the discontinuity quite definitely.

A smooth curve, obtained by averaging these results is shown in (figure 20.) From the area under the curve the latent heat was calculated to be 0.737 calories per mole. Its very small value probably accounts for the difficulties experienced in detecting its presence.

Purity of the Compound:

The cis and trans isomers of decahydronaphthalene were separated by vacuum distillation in a Stedman column of commercial decolin from the Eastman Kodak Co. The cis isomer was then repurified by three recrystallizations until a constant freezing point of $-43.67^{\circ}C$ was obtained.

Table Vl

Specific Heat Determinations - Adiabatic Method.

Run #1		Run #2		Run #3	
Temperature	Specific Heat	Temperature	Specific Heat	Temperature	Specific Heat
45.394	1.7834	44.701	1.7942	43.792	1.7795
45.85	1.7774	45.198	1.7950	44.294	1.7943
46.453	1.7793	45.801	1.7959	44.796	1.7915
47.208	1.7751	46.303	1.7988	45.299	1.7869
47.811	1.7884	46.805	1.8048	45.801	1.7901
48.313	1.7903	47.308	1.8128	46.303	1.7937
48.815	1.7880	47.811	1.8156	46.806	1.7976
49.318	1.7886	48.213	1.8176	47.308	1.8019
49.821	1.7858	48.565	1.8187	47.811	1.8042
50.323	1.7923	48.866	1.8209	48.314	1.8029
50.847	1.7911	49.118	1.8221	48.816	1.8036
51.329	1.7924	49.369	1.8207	49.167	1.8077
51.833	1.8047	49.770	1.8216	49.367	1.8153
52.335	1.8130	50.323	1.8239	49.569	1.8181
53.342	1.7930	51.329	1.8295	49.970	1.8151
53.703	1.8036	51.832	1.8288	50.170	1.8165
		52.336	1.8303	50.374	1.8197
		52.839	1.8304	50.626	1.8197
		53.343	1.8297	50.928	1.8172
		53.847	1.8351	51.229	1.8105
		54.350	1.8360	51.480	1.8139

Table VI (continued)

Temperature	Specific Heat	Temperature	Specific Heat	Temperature	Specific Heat
		54.853	1.8480	51.832	1.8166
		55.355	1.8525	52.335	1.8191
		55.859	1.8527	52.839	1.8247
		56.362	1.8584	53.344	1.8280
		56.865	1.8553	53.796	1.8300
		57.220	1.8541	54.249	1.8379
				54.792	1.8395

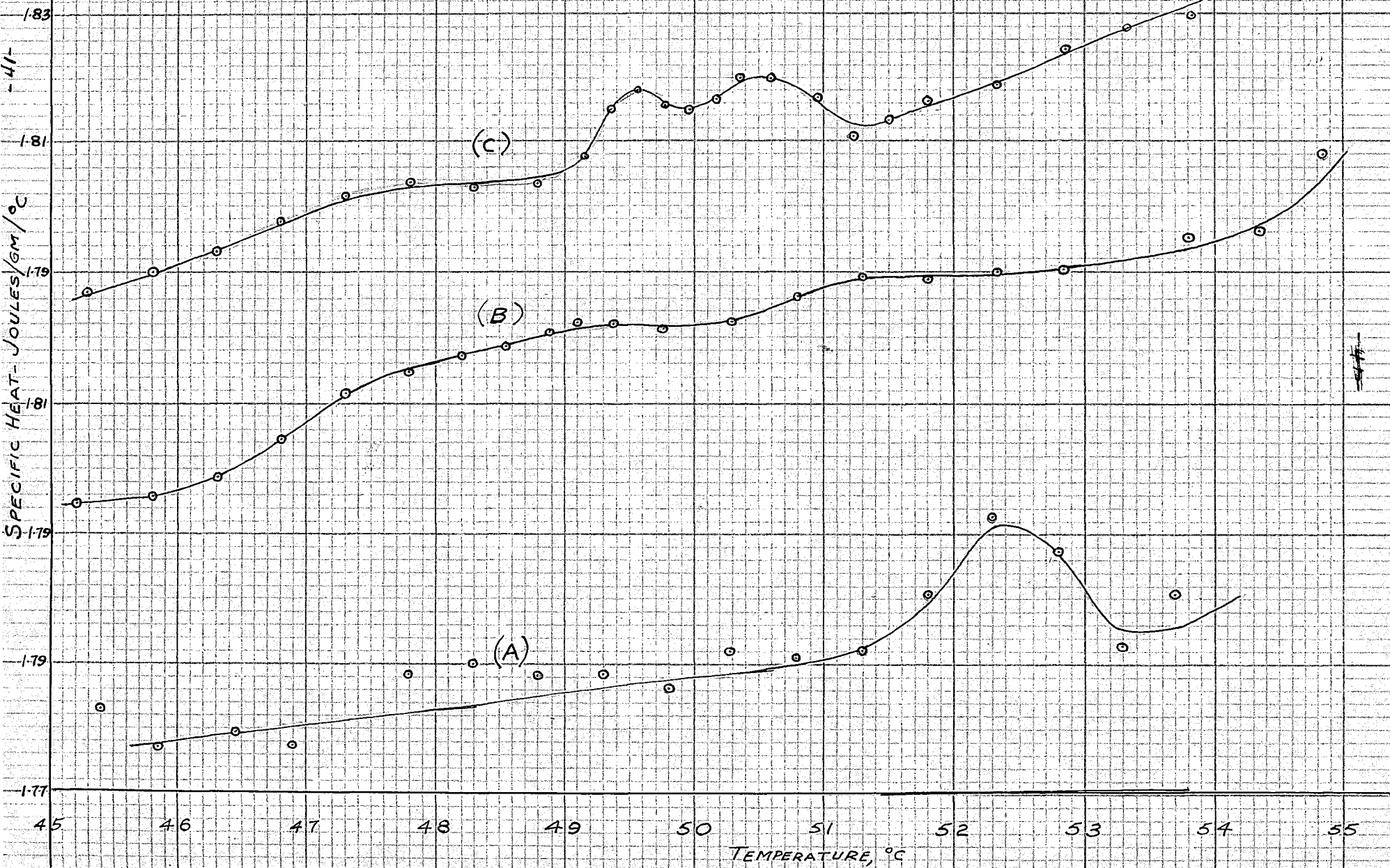Fig 18
Specific Heat of cis Decahydronaphthalene
Adiabatic Method

Table VII

Specific Heat Determination - Isothermal Method.

Run #1

Run #2

Temperature	Specific Heat	Temperature	Specific Heat
47.3	1.8122	49.9	1.821
47.6	1.8128	49.5	1.809
47.8	1.8484	50.0	1.815
48.0	1.8166	50.05	1.839
48.2	1.8056	50.11	1.908
48.6	1.82000	50.15	1.907
48.8	1.8240	50.20	2.728
49.2	1.8135	50.25	2.164
49.6	1.8025	50.31	1.870
49.8	1.8190	50.40	1.771
50.0	1.8294	50.51	1.771
50.2	1.9030	50.63	1.834
50.4	1.8854	50.70	1.834
50.6	1.6641	50.80	1.709
50.8	1.7856	50.9	1.833
51.2	1.8081	51.0	1.833
51.6	1.8115	51.12	1.833
51.8	1.8298	51.22	1.833
52.0	1.8221	51.3	1.832
		51.35	1.832
		51.4	1.832
		51.45	1.766
		51.55	1.831
		51.59	1.831

Fig. 19

Specific Heat of cis Decahydronaphthalene
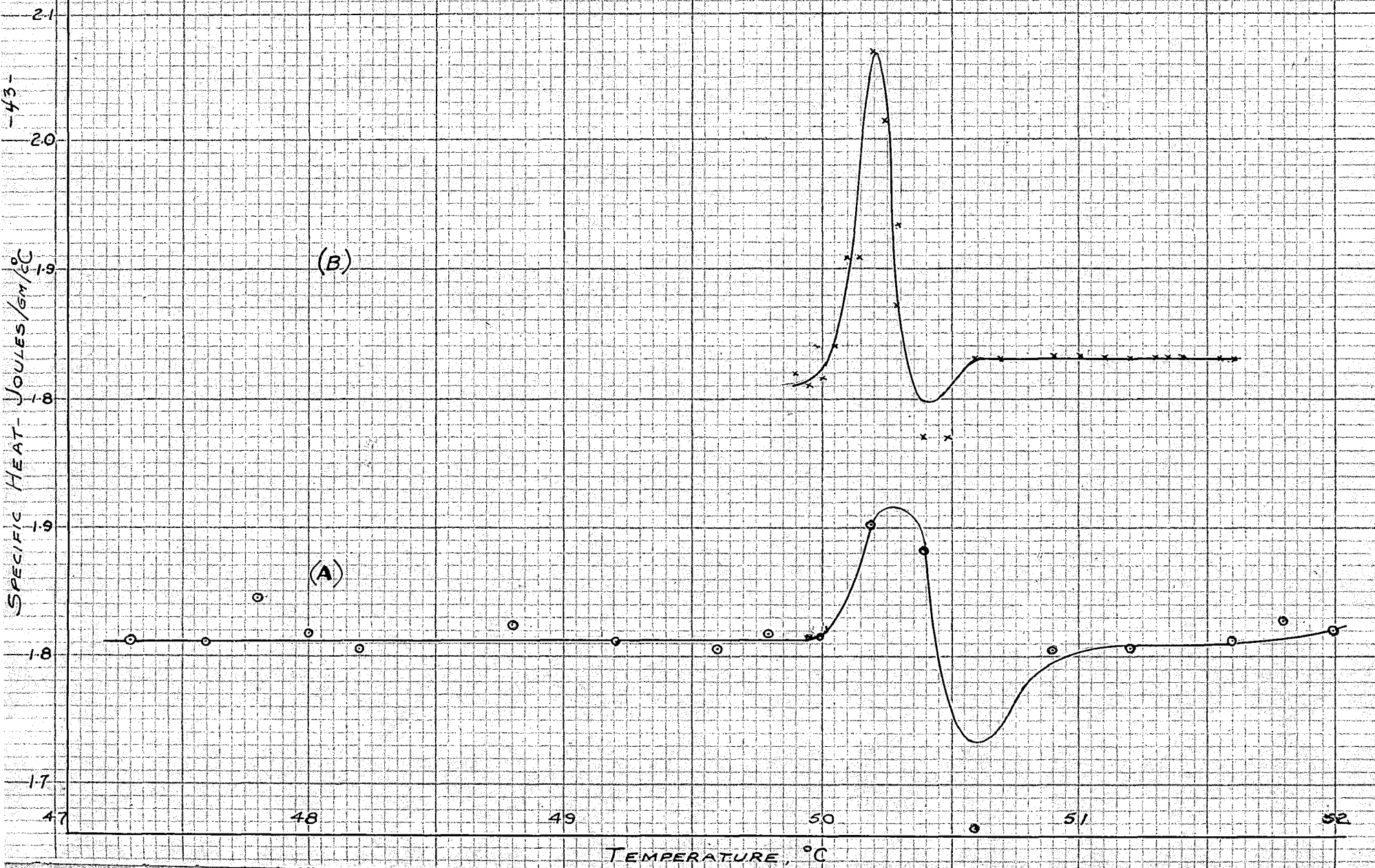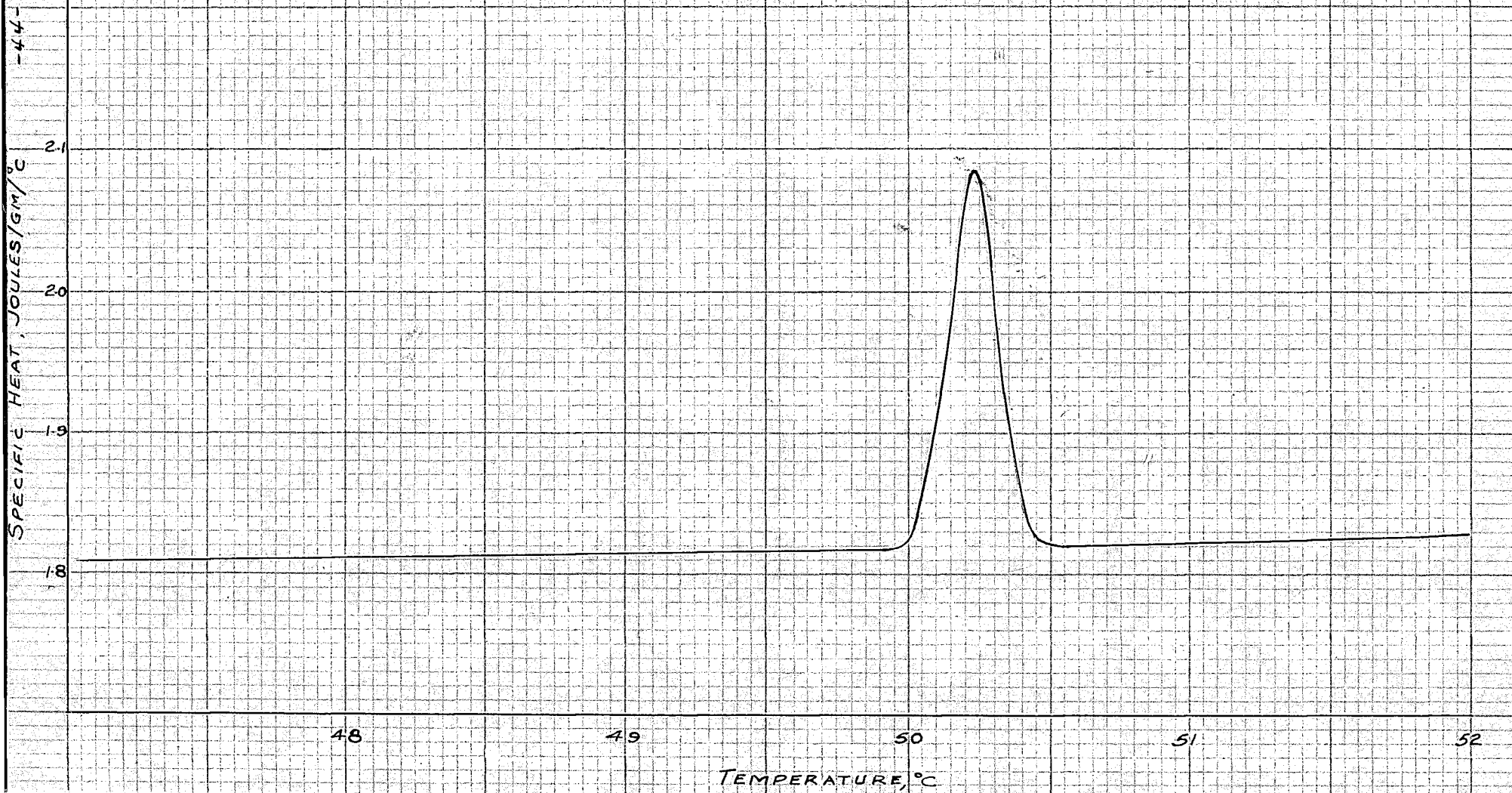
Isothermal Method

Fig 20

Average Specific Heat Curve
for
Cis Decahydronaphthalene
Isothermal Method

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