

THE DENSITIES AND TRANSITION POINTS  
OF CERTAIN LONG CHAIN  
PARAFFIN HYDROCARBONS

by

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## PREFACE

The work described in the following pages is a continuation of the research begun at this university by William Morris in 1936 and further pursued by Eiji Yatabe in 1938-39. As such, this thesis holds no claim to completeness in itself and it should be pointed out that the descriptions given by Morris and Yatabe have not been repeated here except in such cases where repetition was considered necessary for the sake of clarity.

Care has been taken to describe in detail all phases of the work undertaken and although this may appear to have been carried to an extreme at times it is my experience that this will not be considered a failing by those engaged in work of this nature or by those who follow this procedure in filling in the blanks still existing in the paraffin hydrocarbon series.

I wish to acknowledge the valuable assistance and helpful suggestions given by Dr. W. F. Seyer in connection with this research and to express my thanks to Messrs. Bell, Kemper, Leslie, and Morel for the synthesis of certain of the compounds used. I am also indebted to B. J. Mair of the Bureau of Standards, G. W. Stewart of Iowa State University and Dr. Parks of Stanford University for the gift of hydrocarbon samples.

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## TABLE OF CONTENTS

Preface	Page i
Introduction	1
The Structure of Normal Paraffins	1
Preparation and Purification of Hydrocarbons	4
(1) Nonacosane	
(2) Docosane and triacontane	
(3) Octacosane	
Measurement of Densities	8
(1) Theory	
(2) Temperature Control	
(3) Setting up the dilatometer tubes	
(4) Experimental Observations	
(5) Calibration of the tubes	
Results	12
(1) Capillary heights	
(2) Melting points	
(3) Lower transition points	
(4) Upper transition points	

# THE DENSITIES AND TRANSITION POINTS OF CERTAIN LONG CHAIN PARAFFIN HYDROCARBONS

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## INTRODUCTION

The densities and transition points of two hydrocarbons, tetracosane and dotriacontane, have been previously determined in this laboratory by Yatabe and Morris respectively. These data were not considered sufficient basis for generalizations on the paraffin hydrocarbon series and the aim of the present work has been to amass as much more material on this subject as possible and then to attempt a correlation of all results. Octacosane, nonacosane, triacontane, docosane, tetradecane, pentadecane, and hexadecane have been obtained. The first three have been investigated and the values obtained are set forth.

## THE STRUCTURE OF NORMAL PARAFFINS

It has been shown<sup>1</sup> that these hydrocarbons may exist in three forms:

A. The normal form - the crystals are right rectangular prisms and the molecular chains are packed in the cell perpendicular to the base.

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1. A. Müller, Proc. Roy. Soc., London, A138, 516, (1932).

B. A form of lower symmetry - the crystals are no longer rectangular in cross-section and the chains may be tilted relative to the base.

C. A form having rectangular cross-section and chains which are tilted relative to the base.

As these long chain paraffins are heated it is found that at about  $5^{\circ}\text{C}$  below the melting point a definite change in structure takes place as indicated by the sudden change in the 001 spacing of the crystals. A second transformation occurs in a range a few hundredths of a degree below the melting point and again X-ray analysis shows a change in the 001 spacing. Since these structural changes are accompanied by a change in density it is possible to explain them as transitions from one crystal form to another. A consideration of the diagrams of Figure 1 will make this point clear. We will

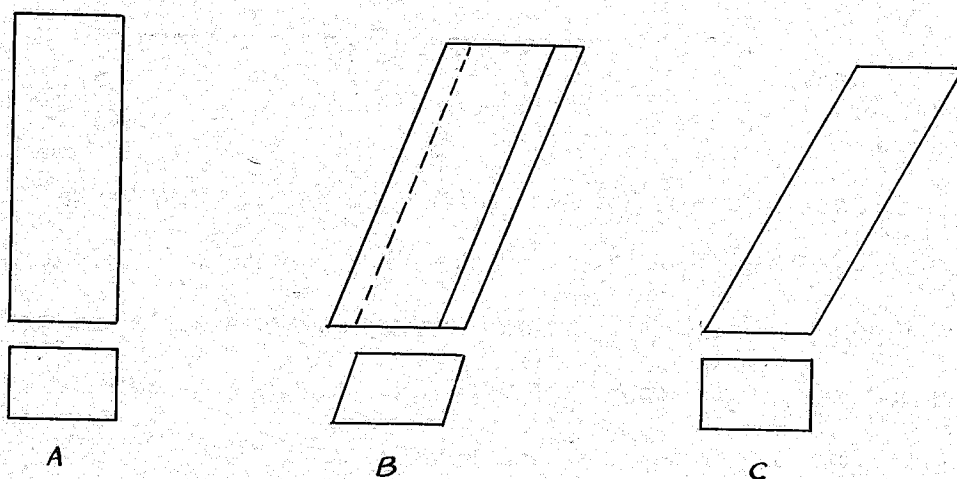


Figure 1

suppose that a hydrocarbon exists in the C form at ordinary temperatures. Now when the lower transition point is reached we find that the density decreases at practically constant temperature, which is exactly what we would expect if the crystal structure changes from the C to the B form, since it is apparent that the volume occupied per molecule has increased. Similarly, if we consider the second transition point as a change from the B to the A form then the further decrease in density experimentally observed is a logical conclusion. That is to say, the above theoretical considerations would lead to a density-temperature curve of the type shown in Figure 2 and this agrees very well with the curve obtained experimentally.

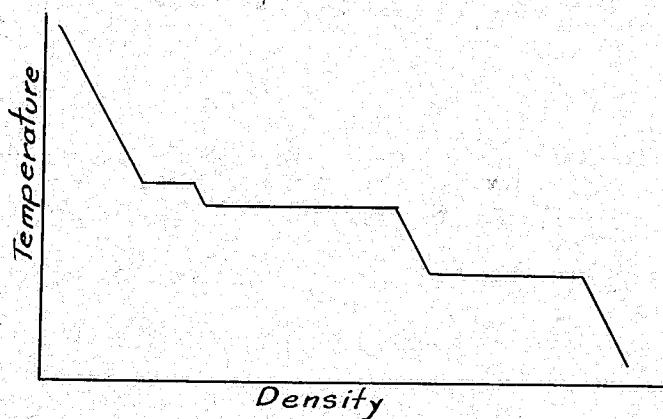


Figure 2

Attempts have been made to explain the reasons for these changes.<sup>2</sup> From a consideration of the heat resisting properties and the general inert character of the paraffin molecule it seems unlikely that temperature should produce any change within the molecule itself and the transition forces must rather be thought of as intermolecular. Crystalline

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2. A. Muller, loc.cit., p.525.

equilibrium may be thought of as dependent upon two factors, attractive forces between molecular chains and attractive forces between end groups. Each of these alone will bring about an equilibrium arrangement of the molecules and a combination of the two may well introduce two positions of equilibrium for the chain depending on the temperature. This explanation is obviously inadequate since it pictures only two forms of higher probability. It has, however, the advantage of agreeing with the gradual nature of the transition as experimentally observed.

#### PREPARATION AND PURIFICATION OF HYDROCARBONS

##### Nonacosane

This hydrocarbon was obtained in the pure state from a sample supplied by the Bureau of Standards. When received this sample had a melting point of approximately  $63.0^{\circ}\text{C}$  as determined with Piper's melting point apparatus. Since Piper and his co-workers<sub>3</sub> give  $63.4\text{--}63.6^{\circ}$  as the melting point of the pure compound, purification was considered necessary. The following is the method used in the recrystallization of nonacosane but the procedure is very similar for all the higher-melting point hydrocarbons.

A small quantity (about 1 gram) of nonacosane was weighed out and placed in a large flask and sufficient glacial acetic acid added to dissolve the hydrocarbon in the neighbour-

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3. Piper et al, Biochem. Jour., 25, 2085, (1931).

hood of its melting point. It was found that nonacosane is approximately 0.05% soluble in glacial acetic acid at 65°. The mixture was warmed and mechanically stirred until the compound was completely in solution. A glass siphon reaching to the bottom of the flask was then substituted for the stirrer and the solution allowed to cool and crystallize. Upon standing the crystals rose to the surface and the underlying mother liquor was siphoned off. Fresh acid was added to the remaining crystals and the above procedure repeated. After eight recrystallizations the crystals were separated from the mother liquor by suction filtration and then transferred with the filter paper to a large beaker of distilled water. By heating the water until the hydrocarbon melted, and then stirring the hot mixture, most of the remaining acetic acid was removed. The nonacosane separated out as a solid surface-layer upon cooling and was transferred to another beaker where it was dissolved in a small quantity of pure ether. The solution was filtered to remove any insoluble material and the purified compound was then reclaimed by evaporation of the ether and final drying in a vacuum desiccator.

The purity of the product was tested by several melting point determinations, using Piper's apparatus.<sup>4</sup> Sample tubes for use with this apparatus were made by drawing out fairly large bore glass tubing to an outside diameter of about one millimetre. Tubing made in this manner is exceptionally thin walled and so is well suited to determinations

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4, E. Yatabe, M.A.Sc. Thesis, U. B. C. (1939), p.3.

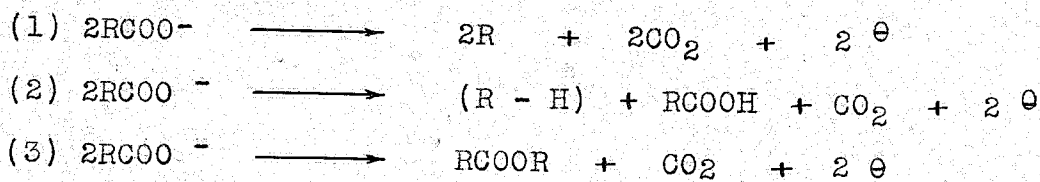


involving heat transfer.

The nonacosane used in density determinations had an average melting point of  $63.5^{\circ}\text{C}$ .

### Docosane and Triacontane

Docosane and triacontane were prepared by the electrolysis of lauric and palmitic acids respectively. The method used was that outlined by Petersen<sup>5</sup> but in a somewhat modified form. The reactions are according to the general equations:



It is only the first reaction which is desired and the others are repressed by the addition of potassium hydroxide.

The original charge consisted of 20 grams of the organic acid, 5 grams of potassium hydroxide, 100 cc. of water and 75 cc. of ethyl alcohol. Electrolysis was then begun at a current density of 2.5 amperes per square decimetre and 5 volts. The temperature was maintained at  $60^{\circ}$  for production of docosane and at  $70^{\circ}$  for triacontane. As the reaction proceeded more acid was added - about 3 grams every two hours - and the volume of the mixture kept constant by the addition of ethyl alcohol and water. The hydrocarbon product collected as an oily layer on the surface and was poured off and set aside for purification with concentrated sulfuric acid<sub>6</sub> and crystalli-

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5. Petersen, Z. Electrochem., 12, 141, (1906).

6. Piper et al, loc.cit., p.2076.

zation from glacial acetic acid. The yield of crude product was about 80 - 85% of the weight of the organic acid used.

The final melting points as determined with the Piper apparatus were and  $65.7^{\circ}$  for the docosane and the triacontane respectively. (cf. Piper's value -  $65.6^{\circ}$  to  $65.8^{\circ}$  for triacontane)

### Octacosane

Octacosane was obtained from myristic alcohol by means of the Fittig reaction. 25 grams of this solid alcohol ( $C_{14}H_{29}OH$ ) were melted in a small flask and hydrogen iodide bubbled into the melt. This gas was generated by the action of water on a mixture of red phosphorus and iodine in the ratio of one to eleven and was passed through water before being led into the alcohol. In this reaction it is important that the air above the alcohol be first displaced as completely as possible to avoid the formation of oxidation products. The reaction was considered complete when all the material in the flask remained liquid upon cooling to room temperature.

A small excess of metallic sodium over that calculated was added to 200 cc. of dry ether and the liquid tetradecyl iodide poured slowly in. The heat of reaction was sufficient to keep the mixture refluxing for several hours after which heating was continued with a steam bath for about six hours. The ether was then evaporated off and 95% ethyl alcohol added to remove excess sodium. Finally the alcohol was removed by evaporation and the crude hydrocarbon purified by ten sulfuric acid treatments and by repeated crystallizations

from acetic acid.

The final melting point obtained was  $61.4^{\circ}$  which is in agreement with Piper's value of  $61.4^{\circ}$ - $61.5^{\circ}$ .

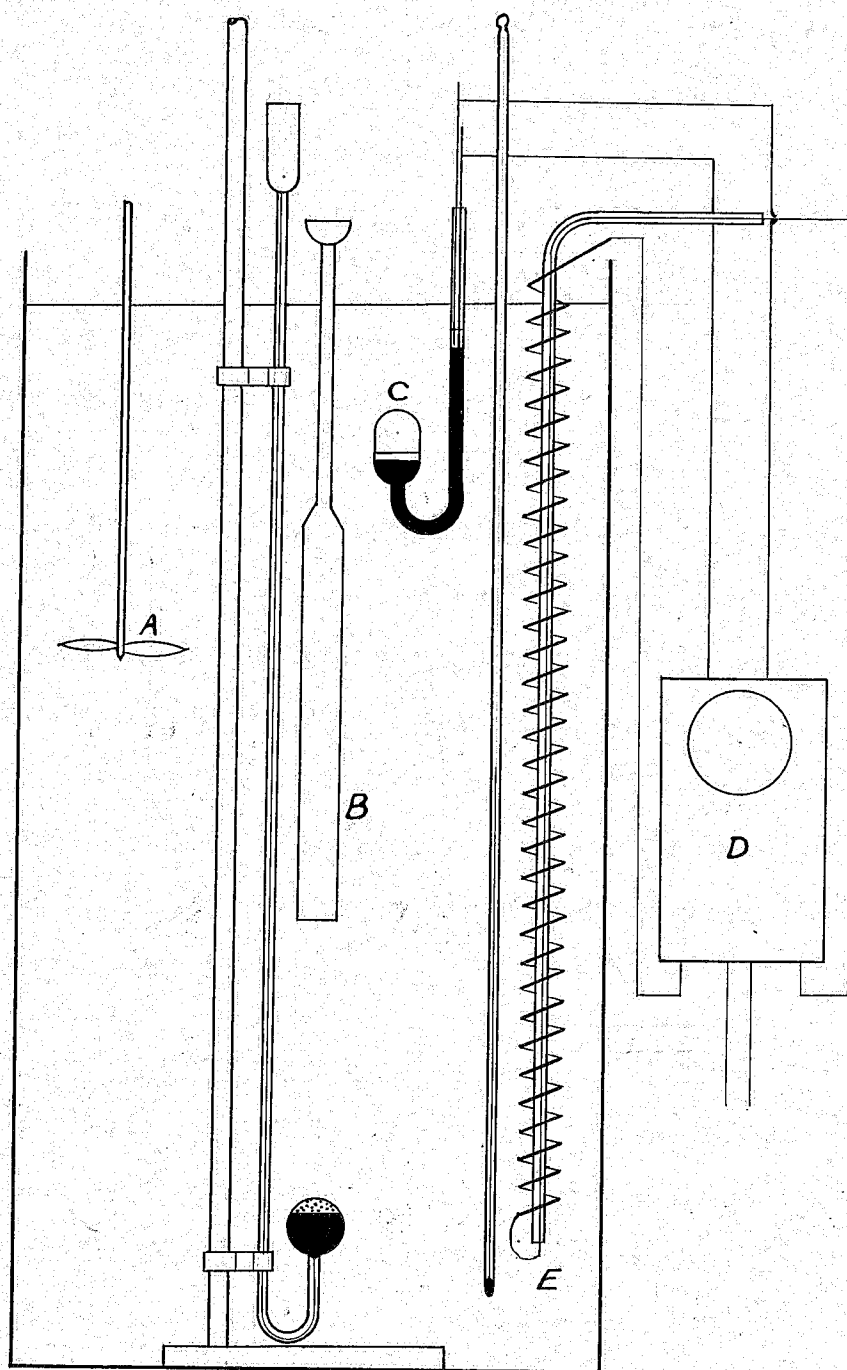
### MEASUREMENT OF DENSITIES

#### Theory

The measurement of densities by the dilatometer method is one of the most accurate means of determining this property. The bulb of the dilatometer tube contains an accurately weighed sample of the hydrocarbon and the remainder of the tube is filled with freshly distilled mercury. The whole tube is immersed in a constant temperature bath. Changes in volume of the compound are reflected in changes of height in the mercury column in the capillary tube. The volume of the mercury and of the apparatus being known it is possible to calculate the density of the hydrocarbon. Suitable corrections must be made, of course, for the expansion of the mercury and for the change in volume of the apparatus with the expansion of the glass. A completely worked example is given with the calculations.

#### Temperature Control

The temperatures at which density measurements were made were held within  $\pm 0.02^{\circ}$  C of the recorded values by immersing the dilatometer tubes in a bath regulated by a precision type thermoregulator. The bath itself consisted of a pyrex glass cylinder 45 cm. high and 25 cm. in diameter, filled



THERMOSTAT ASSEMBLY

FIGURE 3

with water. The bath assembly is shown in the accompanying diagram. (Figure 3) Circulation was obtained with a motor driven stirrer A. Large temperature changes were facilitated by the use of a flat heater B but this was cut out of the circuit entirely when equilibrium was being maintained preparatory to making a density measurement. At these points the temperature was kept constant by the thermoregulator tube C in conjunction with the relay D and the nichrome heating coil E. The electrical connections are shown diagrammatically in Figure 3 but in the actual experimental work the degree of heating was adjusted with a variable resistance coil and several electric lamps. Below room temperature it was necessary to circulate the water through an external copper coil cooled in ice. For this purpose a 110 volt centrifugal pump having a continuous rating of two and a half gallons per minute was used.

#### Setting up the Dilatometer Tubes

Glass bulbs about 2 cm. in diameter were blown from thick walled pyrex tubing and accurately weighed. The purified hydrocarbon sample was melted and approximately 0.7 grams introduced into one of these bulbs through a very small funnel having a slender stem reaching down into the bulb. This sample tube was then connected to a vacuum system and evacuated to about  $1 \times 10^{-4}$  mm. At this pressure the compound was repeatedly melted and allowed to recrystallize in order to free it of occluded gases and any remaining traces of acetic acid or water. This procedure was continued

until the bulb and its contents attained constant weight. (In some cases this may involve keeping the hydrocarbon liquid for a period up to six hours at low pressure since the last traces of impurities are evolved as a slow stream of very minute bubbles.)

The bulb was given a final accurate weighing and then sealed on to the dilatometer tube to which was attached a small, brass zero clip. The completed tube was weighed and then connected to a vacuum mercury still as shown in Figure 4. The whole system was evacuated to a pressure of approximately  $5 \times 10^{-5}$  mm. and mercury was distilled slowly into the tube until enough to fill the bulb and capillary had been added. It was found most convenient to distil an excess of mercury into the tubes and to adjust the volume to the required point by heating the dilatometer to about  $10^{\circ}$  C. above the highest temperature to be investigated and then pouring off the excess mercury. For the purpose of this setting a small glycerin bath is recommended. The completed tube and contained mercury were weighed and then fastened in position in the bath.

All the weighings mentioned in the foregoing were to the nearest 0.1 mg. and were corrected for the buoyant effect of air.

#### Experimental observations

The only experimental measurements required are the temperatures and the corresponding capillary heights. The former were obtained from an ordinary mercury thermometer

graduated in tenths. This had been previously calibrated against a platinum resistance thermometer at various temperatures and found to have an accuracy of  $\pm 0.03^{\circ}$  C over the range used in this work. Capillary heights were measured with a Gaertner cathetometer graduated in 0.005 cm. In making these latter readings the mercury columns were illuminated from behind the bath with electric lamps.

In order that the hydrocarbon reach its final state at any one temperature it was necessary to maintain the thermostat at that temperature for at least three hours before the cathetometer readings were made. In the neighbourhood of the melting and transition points a much longer time may be required - in some cases about 48 hours. It was found, in general, that the finer the temperature was controlled, the quicker a steady state was reached.

#### Calibration of the Tubes

When a complete set of measurements had been made, the dilatometers were taken from the bath and the mercury and hydrocarbons removed. This was accomplished by applying vacuum and then repeatedly washing with hot 95% ethyl alcohol to dissolve out the hydrocarbon. The tubes were then dried, evacuated, and filled with mercury as before. They were then weighed and again fastened in place in the thermostat. A series of measurements of capillary heights was made and from the known mass of the mercury it becomes possible to calculate the volume of the dilatometers, including the bulb and capillary, for any desired height above the zero clips. If the

tubes are of uniform bore the cross-sectional area may be determined and used in later calculations.

### RESULTS

From the discussion already given of the dilatometer method it will be obvious that if the capillaries are of uniform bore the general shape of the density-temperature curves can be obtained immediately by plotting capillary heights against temperature. As the possibility of serious impurity always exists, the value of such curves should not be under-estimated since they will show up any large discrepancies and indicate whether or not it will be of value to perform the calibrations and enter into the calculation of the densities.

In Table I the temperatures and corresponding capillary heights for octacosane, nonacosane, and triacontane are given. In Figure 5 immediately following, these are plotted, together with the temperature-density curves obtained for tetracosane and dotriacontane.<sup>7</sup>

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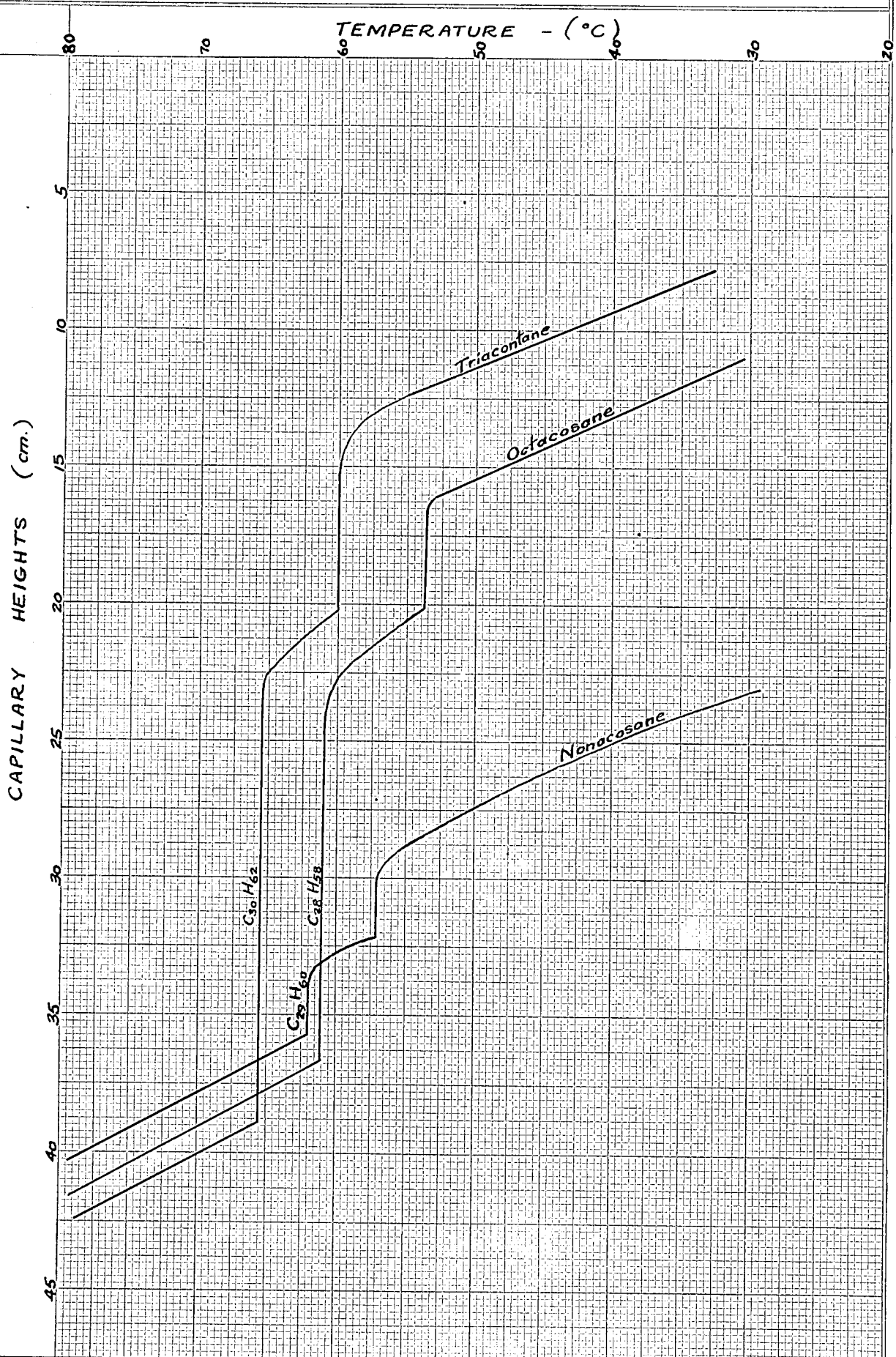
7. E. Yatabe, loc.cit., and W. Morris, M.A.Sc. Thesis, U. B. C., (1938).



TABLE I

<u>Temp.</u>	<u>Octacosane</u> Height - cm.	<u>Nonacosane</u> Height - cm.	<u>triacontane</u> Height - cm.	<u>Sensitive</u> <u>Liquid</u>
35.0	12.070	23.895	8.200	Ethyl ether
40.0	13.095	24.980	9.180	
45.0	14.240	26.090	10.295	
48.0	14.930	26.810	10.940	
51.0	15.675	27.590	11.630	Carbon disulfide
52.0	15.895	27.895	11.840	
53.0	16.100	28.230	12.055	
54.0	20.160	28.500	12.275	
55.0	20.595	28.800	12.355	Acetone
55.5	20.800	28.845	12.460	
56.0	20.995	28.860	12.575	
56.5	21.165	28.990	12.790	
57.0	21.360	30.030	12.810	
57.5	21.535	32.025	12.945	
58.0	21.705	32.025	13.070	
58.5	21.935	32.565	13.175	
59.0	22.120	32.565	13.565	Chloroform
59.5	22.340	32.625	14.265	
60.0	22.675	32.710	20.160	
60.5	23.310	32.905	20.465	
61.0	27.82-28.92	33.100	20.695	
61.2	36.595	33.100	20.765	
61.4	36.645	33.165	20.850	
62.0	36.820	33.475	21.090	
62.5	36.955	33.600	21.290	Methyl alcohol
63.0	37.095	35.78-35.93	21.475	
63.2	37.155	36.345	21.550	
64.0	37.370	36.530	21.870	
64.5	37.510	36.650	22.115	
65.0	37.645	36.760	22.695	
65.2	37.705	36.805	24.035	
65.4	37.760	36.845	38.885	
65.5	37.790	36.900	38.920	Carbon tetrachloride
65.6	37.825	36.925	38.955	
65.7	37.845	36.950	38.980	
65.8	37.875	36.980	39.005	
66.0	37.940	37.045	39.080	Ethyl alcohol
68.0	38.480	37.480	39.580	
70.00	39.040	37.965	40.115	
75.0	40.410	39.130	41.480	

# FIGURE 5



An examination of Table I and of the curves in Figure 5 shows the following results:-

(2) The melting points are in all cases somewhat lower than those determined with the Piper apparatus. This is to be expected, however, as the rate of heating is here very much smaller. For the same reason the dilatometer method would be expected to yield low melting points in all cases and this appears to be true. For octocosane Hildebrand and Wachter<sup>8</sup> give an average value of  $62^{\circ}$  for the melting point and their curve shows a minimum recorded value of  $60^{\circ}$ . The value obtained in this work is  $61.2^{\circ}$ . For nonacosane the average is  $64^{\circ}$  with a minimum of  $62.5^{\circ}$  in comparison with  $63.3^{\circ}$  determined with the dilatometer. Triacontane shows an average of  $66.0^{\circ}$ , minimum  $65.6^{\circ}$ , and dilatometer  $65^{\circ}$ . It is not felt that the low values obtained herein are a result of impurities, as the hydrocarbons were in all cases recrystallized to constant melting point from glacial acetic acid and treated with all possible care in charging the dilatometers. In view of the fact that the three hydrocarbons were each prepared by a different method and that the scheme for purification was somewhat different in the three cases, it again seems more likely that these consistent low values are a result of the method of measuring.

(3) The first transition points on heating were obtained for the three compounds. In each case the transition was accompanied by an abrupt change in volume, confirming the explanation of this transformation as a change from the C to the A

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8. Hildebrand and Wachter, J. Am. Chem. Soc., 51, 2487 (1929).

form of crystal structure.<sup>9</sup> It must be noted, however, that it would serve equally well if the transition were from B to A form.<sup>10</sup> This matter is discussed later where densities can be used to indicate the actual nature of the change. The transition temperatures determined are  $53.8^{\circ}$ ,  $57.1^{\circ}$ , and  $60.0^{\circ}$ , for  $C_{28}H_{58}$ ,  $C_{29}H_{60}$ , and  $C_{30}H_{62}$  respectively.

It will be noticed that the slopes are very steep at these transition points. This again seems to confirm the assumption of purity made above.

(4) The second transition - i.e., from the translucent to the opaque form - was observed in the samples very near their melting points. The exact temperatures were not determined as it was found impossible to maintain the thermostat any closer than  $\pm 0.02^{\circ}$  over a long period of time due to the effect of changing barometric pressure on the thermoregulator and the adjustments which this necessitates. In this case the transition does not seem to be accompanied by any appreciable change in volume.

(5) In Figure 6 melting points and lower transition points are plotted against the number of carbon atoms. In both cases the values obtained by Morris and by Yatabe have been included. It will be seen that the melting points fall very nearly along a smooth curve. The values for melting points of other hydrocarbons taken from this curve are in good agreement with those found in the literature.<sup>11</sup>

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9. Piper et al, loc.cit., p.2080.

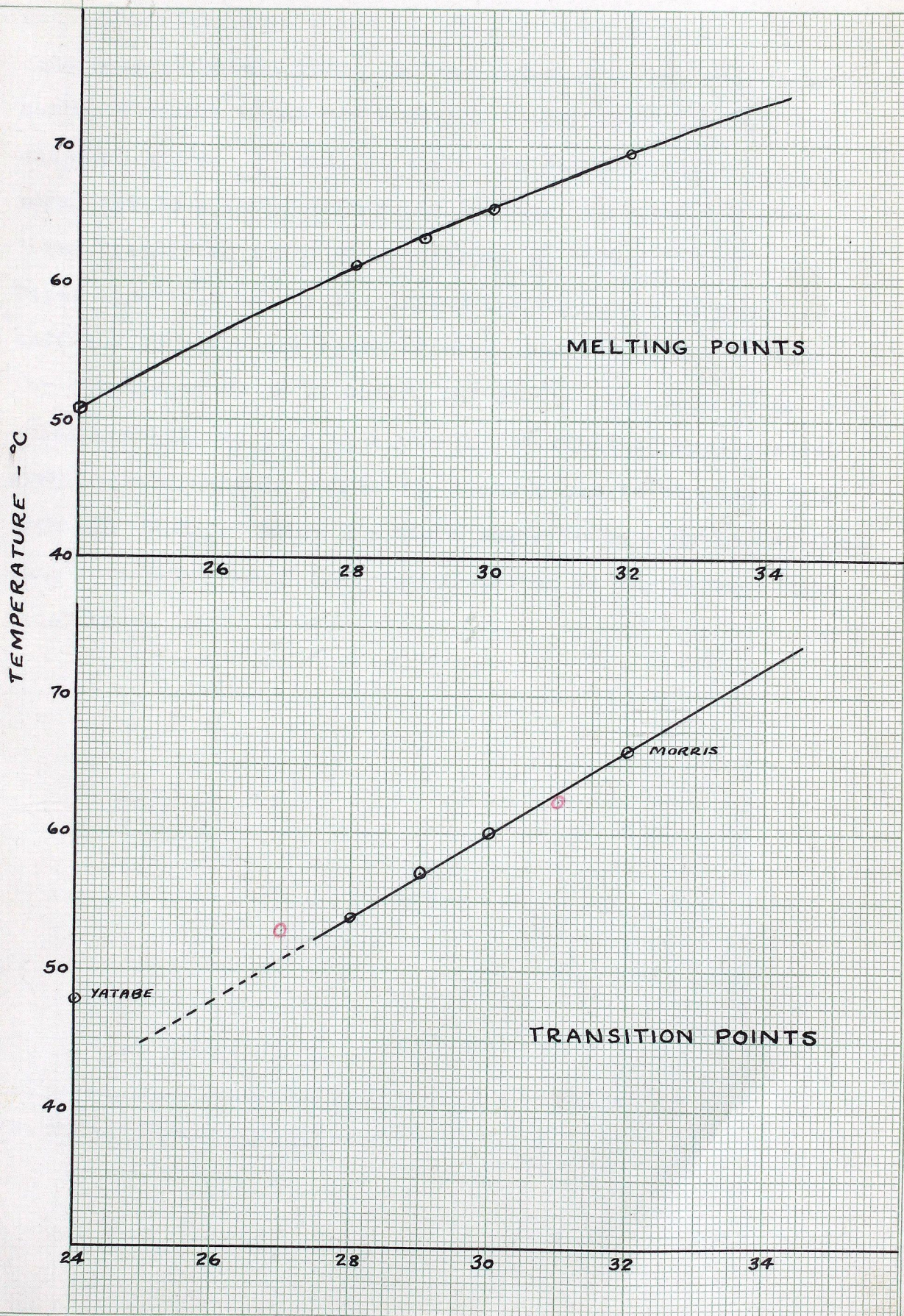
10. E. Yatabe, loc.cit., p.15.

11. Hildebrand and Wachter, loc.cit.; Piper et al., loc.cit., p.2080; Krafft, Ber., 19, 2219, (1886).



# FIGURE 6

No. of CARBON ATOMS





The plot of lower transition points (heating) does not agree with Piper's results<sub>12</sub> on the same question. He considers it necessary to use two lines, one for the even-numbered carbon atoms and a second, lower line for the odd-numbered atoms. It will be seen from Figure 6 that in this work, due to a large difference between the value for the lower transition point of octacosane as determined by the Piper apparatus and by the dilatometer method, a single line suffices to place all these points. Assuming Piper's value for octacosane to be in error, but at the same time using his other results, we find that within the limit of experimental error the transition points lie along a single straight line from C<sub>27</sub> to C<sub>34</sub>. Below C<sub>27</sub> there seems to be a deviation from this rule which would bear investigation by the methods outlined here.

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12. Piper et al, loc.cit., p.2082.

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