* THE DENSITY AND TRANSITION POINTS *

OF

* N-TETRACOSANE *

A THESIS SUBMITTED FOR THE DEGREE

OF

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THE DENSITY AND TRANSITION POINTS

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N-TETRACOSANE

I. INTRODUCTION

It has been known from X-ray studies and other investigations that solid paraffins, in common with other long-chain carbon compounds, exhibit sudden transformations in their crystal structure as they are passed through certain temperature ranges near their melting points.

According to A. Müller,[1] there are three types of paraffin crystals known so far:

(A) The normal form, in which the chains are packed in a prismatic cell of rectangular cross-section. The chains are perpendicular to the base of the cell.

(B) A form of lower symmetry, in that the chains may be tilted relative to the base, which is not rectangular.

(C) A form which has a rectangular cross-section and chains which are tilted relative to the base.

These forms are illustrated below:

A.   B.   C.

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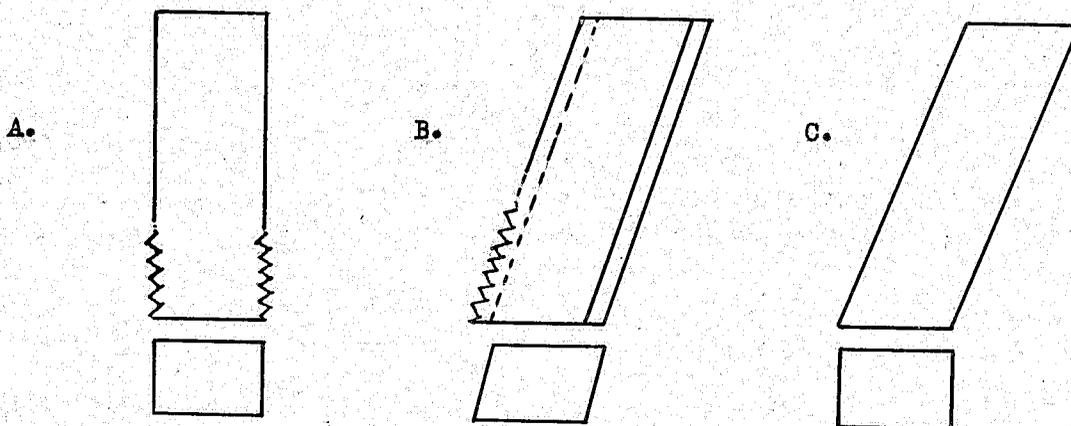
[1]Müller, Proc. Roy. Soc., London., 138 A, 514, (1932).

X-ray measurements show that the length of the chain axis depends much less upon the temperature than the other two axes which are contained in the plane of the base. Müller, in measuring the expansion of these axes in the A and C forms, found that an abrupt transition took place for tetracosane ($C_{24}H_{50}$) and all the higher members of the series. One object of this present work was to determine whether or not this transition affected the density of the hydrocarbons.

S.H. Piper and his associates have shown that at or near this transition point studied by Müller there is also a change in the molecular tilt, which may or may not be reversible upon cooling.[2] This change is shown by the large increase in the 001 spacing when studied by X-rays. This can also be seen when a small sample of a paraffin is heated in a melting point apparatus, (Fig. 1) in which case there is a definite change in the opacity and volume of the substance. Since there is a density change involved in this transition, the dilatometer method was adopted last year by W.M. Morris[3] of this laboratory who determined the density and transition points of n-dotriacontane (dicetyl). The present work is an investigation of the similar properties of n-tetracosane, employing the same type of apparatus.

[2] Piper et al, Biochem. J., 25, 2083 (1931).
[3] Morris, M.A.Sc. Thesis, U.B.C. (1938).

II. EXPERIMENTAL PROCEDURE

(1) Preparation and Purification of Tetracosane.

The n-tetracosane had been previously prepared by H.P. Godard of this laboratory for his research on the solubility of tetracosane in various solvents.[4] It had been synthesized from Eastman Kodak Company lauryl alcohol, using Krafft's method,[5] employing the Wurtz-Fittig reaction.

It was purified by repeated fractional crystallization from glacial acetic acid, followed by washing with distilled water and drying in a vacuum desiccator. The procedure was continued until a constant melting point was obtained.

The preparation was quite pure,[4] so that one of the samples was recrystallized only once. The other sample was recrystallized fourteen times.

(2) Determination of the Melting Point.

The apparatus was the same type as that employed by Piper,[6] consisting of a small glass bulb, containing about 100 c.c. of concentrated sulphuric acid. (see Fig. 1) The temperature was raised slowly by a small burner, and was read off a calibrated thermometer which was graduated in tenths of a degree. The usual stem correction was applied, using the equation,

$$T_c = T_0 + 0.000156 \ L \ (T_0 - T_m)$$

where T_c = corrected temperature,

          T_0 = observed temperature,

[4] Godard, M.A. Sc. Thesis, U.B.C. (1937).
[5] Krafft, Ber., 19, 2219 (1886).
[6] Piper et al (loc. cit. p. 2081).

Correction
Thermometer

Calibrated Thermometer

Conc. H_2SO_4

Tetracosane.
Sample.

Asbestos
Board.
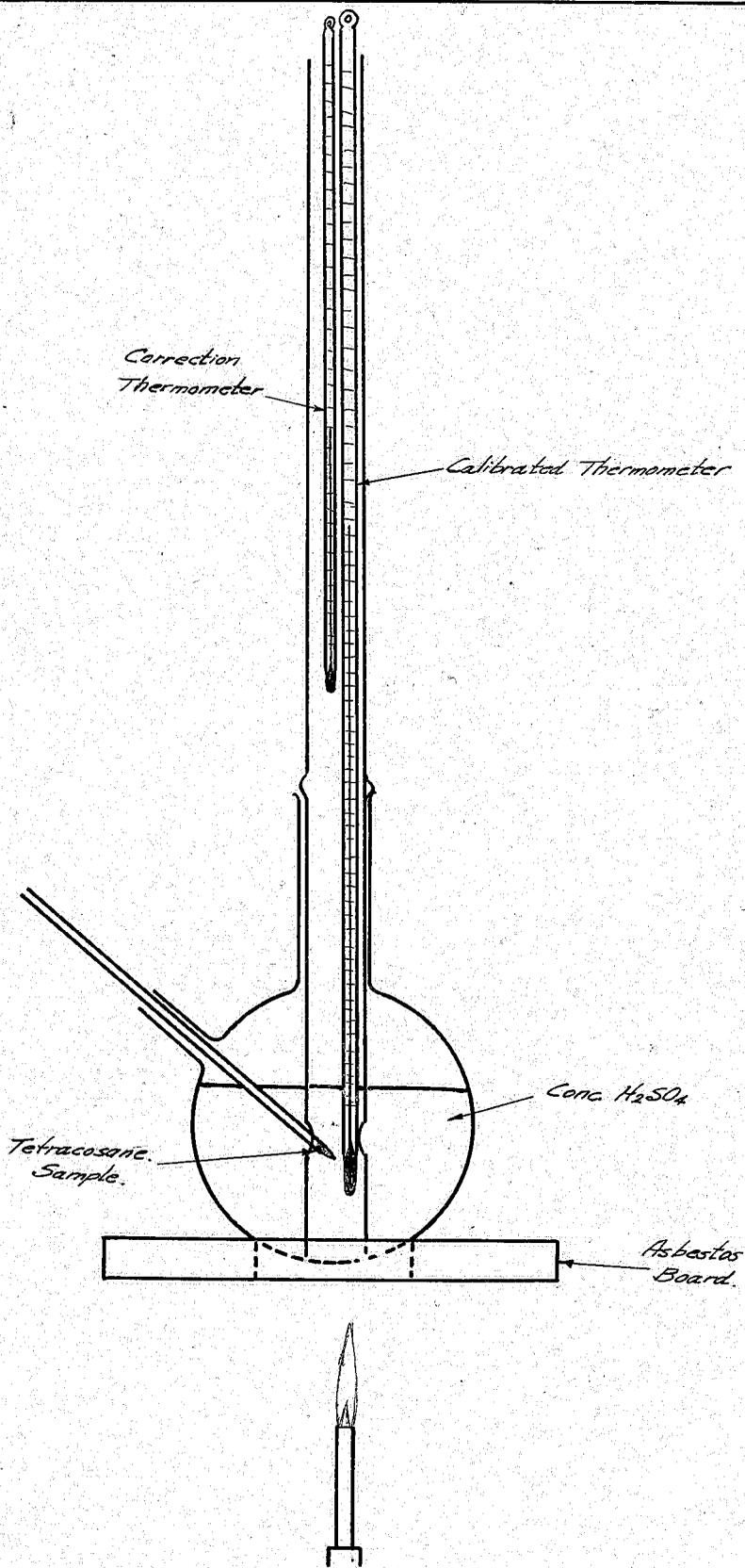
Fig. 1   Melting Point Apparatus

L = length in degrees of mercury column not at temp-
erature to be measured,

T_m = temperature of the middle point of the emergent
thread.

It was possible with care to repeat melting points within an accuracy of
0.1°C. By taking care not to raise the temperature at a rate faster than
0.5° per minute, it was found that the melting point of tetracosane was
50.7° - 50.8°C. Although this melting point was lower than the values
obtained with methods employing more rapid rates of heating, it was in
accordance with Piper's assertion that his method gave results 0.5° -
0.7° lower than the others.[6] The recorded values of the melting point of
n-tetracosane vary from 51.0°,[7] 51.1°[8] to 51.5°C.[9]

A second method for the determination of the melting point using the
dilatometer and thermostat has been discussed elsewhere. This method
gave the melting point as 50.7°C.

(3) The Preparation of the Dilatometer.

The dilatometer tubings used last year by W.M. Morris[10] were employed
again this year. These pyrex capillary tubings had been found to be of
uniform cross-section by measuring, at a constant temperature, the length
of a given amount of mercury at different points along the tubings. Know-
ing the mass, and hence the volume of the mercury, it was possible to cal-
culate the cross-sectional area of a tubing. The cross-sectional areas
of the tubings used for this present work were 0.00343 sq. cm. and 0.00521
sq. cm., when calculated by this method.

[6]Piper et al (loc. cit. p. 2081).
[7]Hildebrand, J.A.C.S. 51, 2487 (1929).
[8]Beilstein, Org. Chem., Vol. I (p. 107) (1893).
[9]Krafft, (loc. cit.).
[10]Morris, (loc. cit.).

Now, a thick-walled bulb of about 2 cm. diameter was blown from a piece of strong pyrex tubing and was weighed accurately. About 0.7 gm. of tetracosane was weighed out, melted, filtered, and then poured into the bulb by means of a small funnel, whose end was drawn. The bulb was then attached to a system evacuated to .00005 mm. and the hydrocarbon was repeatedly melted and solidified to remove all occluded solvent and gases. This procedure was repeated until a constant weight was obtained. The bulb was now sealed to the 0.00521 sq. cm. dilatometer tubing, the brass zero-point clip was attached near the bottom, and the completed dilatometer was weighed. The dilatometer was now attached to the vacuum system, evacuated to the same order as before, and mercury was distilled in. When sufficient mercury had been distilled over the dilatometer was removed, and then weighed again. All the weights were recorded to the nearest 0.1 mg. and corrected for the buoyancy of the air.

(4) The Use of the Dilatometer.

The dilatometer was now clamped vertically to a weighted brass rod, and placed in the thermostat (Fig. 2) which consisted of a cylindrical pyrex glass vessel containing water electrically heated by a coil of nichrome wire controlled by a precision type thermo-regulator. Good agitation was obtained with a propellor-type stirrer. The temperature was controlled to within 0.02° in the range 30°-75°C, by means of this arrangement. For lower readings, the temperatures were held constant manually by an adjusted flow of ice water.

The height of the mercury level above the zero point mark at various temperatures was measured by means of a cathetometer, graduated in 0.005 cm. All the readings were taken after the temperature had been kept constant for from 3 hours to 75 hours, depending on the temperature. For
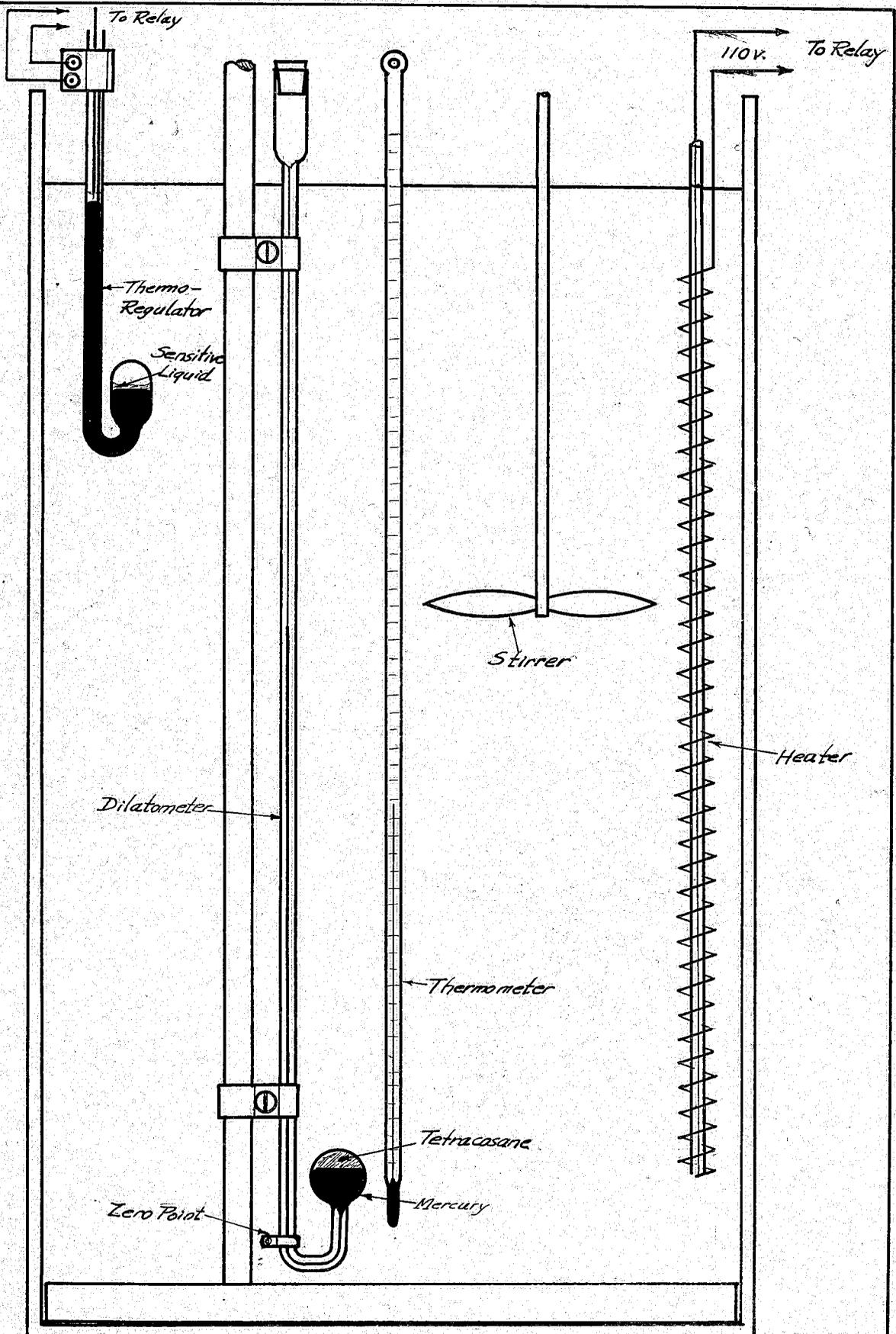
Fig.2   Diagram of Thermostat

temperatures very near the transition points, it was found necessary to keep the temperature constant for 24 hours or more, in order that equilibrium was to be reached. Most of the readings were duplicated, whether they were obtained by heating or cooling the bath. The temperatures were read off the calibrated thermometer placed totally immersed in the bath.

It was found necessary to add some more mercury for the low temperature readings. This was corrected for in the density calculations.

For the tubing of 0.00343 sq. cm. cross-sectional area, about 0.5 gm. of tetracosane was required.

To determine the melting point of tetracosane by using the dilatometer and the thermostat, the temperature was raised to $50.4^{\circ}C$. and kept there for 3 hours, then raised 0.1° every 3 hours. It was found that the hydrocarbon melted completely at $50.7^{\circ}C$. after 2 hours, which agreed very well with the value obtained previously.

(5) <u>Calibration of the Dilatometer.</u>

The mercury and hydrocarbon were removed from the dilatometer. The mercury was removed by applying vacuum, and the hydrocarbon by repeated washing with hot 95% ethyl alcohol. After making sure that all the hydrocarbon was removed, the dried dilatometer was weighed and then attached to the vacuum system. Mercury was distilled into it, completely filling the bulb. After weighing, it was placed in the thermostat and the height of the mercury column was measured at various temperatures. Knowing the mass of the mercury, the volume of the mercury was easily determined as was the cross-sectional area of the capillary tubing, which value agreed excellently with that obtained by the first method.

III.   RESULTS

   In the following tables and discussions, Sample 1 refers to the tetracosane which had been recrystallized once from Godard's preparation, (loc. cit.) while Sample 2 refers to that which had been recrystallized 14 times.

(1') Calibration of Tubes by the Second Method.

   Sample calculations for the two tubings are given:

Sample 1.

Mass of Mercury	—	47.2891 gm.
Volume at 50°C.	—	3.50988 c.c.
Volume at 30°C.	—	3.49727 c.c.
Difference in Volume	—	0.01261 c.c.

Correction for Expansion of Glass

$$= (20)(3.49727)(0.0000096) = 0.00067 \text{ c.c.}$$

Net expansion of Mercury   —   0.01194 c.c.

Difference in Levels = 7.820 – 5.530 = 2.290 cm.

   Area = 0.01194/2.290 = 0.005214 sq.cm.

Volume of Bulb to Zero-Point at 30°C.,

$$V_{30}^{0} = V_{30}^{h} - hA = 3.49727 - 5.530(0.005214)$$

$$= 3.46844 \text{ c.c.}$$

Sample 2.

Mass of Mercury	—	63.3057 gm.
Volume at 50°C.	—	4.69873 c.c.
Volume at 30°C.	—	4.68179 c.c.
Difference in Volume	—	0.01695 c.c.

Correction for Expansion of Glass

$$= (20)(4.68179)(0.0000096) = 0.00090 \text{ c.c.}$$

Net Expansion of Mercury   -   0.01605 c.c.

Difference in Levels = 11.275 - 6.585 = 4.690 cm.

Area = 0.01605/4.690 = 0.003422 sq. cm.

Volume of Bulb to Zero-Point at 30°C. ,

$$V_{30}^{o} = V_{30}^{h} - hA = 4.68179 - 6.585(0.003422)$$

$$= 4.65926 \text{ c.c.}$$

The values are tabulated in Table I below:

TABLE I.

Sample	Temperature	Area of Capillary	Volume at Zero Pt.
1	30° C.	0.005214 sq. cm.	3.46844 c.c.
2	30° C.	0.003422 sq. cm.	4.65926 c.c.

The areas of the capillary tubings computed by the above method are seen to agree very well with the values obtained by the first method, viz., 0.00521 sq. cm. and 0.00343 sq. cm. .

(2) Calculation of Densities.

Since all the calculations follow the same pattern, only one example has been given. The following symbols were used:

A - cross-sectional area of the tube.

t - temperature at which reading was taken.

V_{30}^{o} - volume of bulb at the zero mark, the subscript indicating the temperature, 30°C., at which the volume was determined.

h - height of mercury column above zero mark.

V_{30}^{h} - volume at height h at 30°C. .

V_{t}^{h} - volume at height h at t°C.

- $V_{30}^{h}(1 + a(t - 30))$ where a = 9.6 x 10^{-6} c.c./ °C.,
        the coefficient of cubical expansion of pyrex glass.

W — mass of mercury in the bulb.

V_t — volume of mercury in the bulb at t^oC.

   — W X (Specific Volume of Mercury at t^oC.)

w — mass of tetracosane in the bulb.

v_t — volume of tetracosane in the bulb at t^oC.

   — $V_t^h - V_t$

D_t — density of tetracosane at t^oC.

   — w / v_t

Example

t — 50.90^o C.

A — 0.005214 sq.cm.

h — 32.665 cm.

hA = (0.005214)(32.665) = 0.17032 c.c.

V_{30}^o — 3.46844 c.c.

V_{30}^h = 3.46844 + 0.17032 = 3.63876 c.c.

$V_{50.90}^h$ = 3.63876(1 + (9.6 X 10^{-6})(50.90 - 30.00))

     = 3.63949 c.c.

W = 36.6789 gm.

$V_{50.90}$ = 36.6789(0.07423506) = 2.72287 c.c.

$v_{50.90}$ = 3.63949 - 2.72287 = 0.91662 c.c.

w = 0.7137 gm.

$D_{50.90}$ = 0.7137 / 0.91662 = 0.7786 gm. / c.c.

The results for the two samples for the complete temperature range are as follows:

TABLE II

Sample 1.

V_{30}^o — 3.46844 c.c.

A — 0.005214 sq. cm.

w — 0.7137 gm.

W — 36.6789 gm.

t	h	hA	V^h_{30}	V^h_t	V_t	v_t	D_t
30.00	1.340	0.00699	3.47543	3.47543	2.71259	00776284	0.9356
35.00	2.050	0.01069	3.47913	3.47930	2.71505	0.76425	0.9339
40.00	2.590	0.01350	3.48194	3.48227	2.71751	0.76476	0.9332
42.00	3.155	0.01645	3.48489	3.48529	2.71874	0.76655	0.9311
45.00	3.560	0.01856	3.48700	3.48750	2.71996	0.76754	0.9299
46.00	4.220	0.02200	3.49044	3.49098	2.72045	0.77053	0.9262
46.60	5.175	0.02698	3.49542	3.49598	2.72075	0.77523	0.9206
46.80	5.550	0.02883	3.49727	3.49783	2.72084	0.77699	0.9185
46.90	5.885	0.03068	3.49912	3.49969	2.72089	0.77880	0.9164
47.00	6.380	0.033327	3.50171	3.50228	2.72094	0.78134	0.9134
47.10	7.855	0.04096	3.50940	3.50998	2.72099	0.78899	0.9046
47.20	8.495	0.04429	3.51273	3.51331	2.72104	0.79227	0.9008
47.40	9.910	0.05167	3.52011	3.52070	2.72114	0.79956	0.8926
47.50	10.510	0.05480	3.52324	3.52383	2.72119	0.80264	0.8892
47.60	10.630	0.05542	3.52386	3.52445	2.72124	0.80321	0.8886
47.70	13.350	0.06961	3.53805	3.53865	2.72129	0.81736	0.8732
47.80	13.900	0.07247	3.54091	3.54152	2.72134	0.82018	0.8702
47.90	14.385	0.07500	3.54344	3.544055	2.72139	0.82266	0.8676
48.00	14.440	0.07529	3.54373	3.54434	2.72143	0.82291	0.8673
48.30	14.550	0.07586	3.54430	3.54492	2.72158	0.82334	0.8668
49.00	14.780	0.077086	3.54550	3.54615	2.72194	0.82421	0.8659
49.30	14.885	0.07761	3.54605	3.54671	2.72209	0.82462	0.8655
50.00	15.130	0.07983	3.54827	3.54895	2.72242	0.82653	0.8635

t	h	hA	v_{30}^h	v_t^h	V_t	v_t	D_t
50.30	15.435	0.08048	3.54892	3.54961	2.72257	0.82704	0.8630
50.50	15.875	0.08277	3.55121	3.55191	2.72267	0.82924	0.8607
50.60	18.255	0.09518	3.56362	3.56433	2.72272	0.84161	0.8480
50.70	32.615	0.17005	3.63849	3.63921	2.72277	0.91644	0.7788
50.80	32.645	0.17021	3.63865	3.63937	2.72282	0.91655	0.7787
50.90	32.665	0.17032	3.63876	3.63949	2.72287	0.91662	0.7786
52.00	32.925	0.17167	3.64011	3.64088	2.72341	0.91747	0.7779
55.00	33.625	0.17532	3.64376	3.64464	2.72487	0.91977	0.7760
56.00	33.865	0.17657	3.64501	3.64592	2.72537	0.92055	0.7753
60.00	34.805	0.18147	3.64991	3.65096	2.72733	0.92363	0.7727
65.00	35.990	0.18765	3.65609	3.65732	2.72978	0.92754	0.7694
70.00	37.155	0.19373	3.66217	3.66357	2.73225	0.93132	0.7663
75.00	38.350	0.19996	3.66840	3.66998	2.73470	0.93528	0.7631
		With Additional Mercury		W − 37.2142 gm.			
5.00	5.220	0.02722	3.49566	3.49482	2.73974	0.75508	0.9452
10.00	5.930	0.03092	3.49936	3.49869	2.74223	0.75646	0.9435
15.00	6.630	0.03457	3.50301	3.50251	2.74472	0.75779	0.9418
20.00	7.215	0.03762	3.50606	3.50572	2.74721	0.75851	0.9409
25.00	7.865	0.04101	3.50945	3.50928	2.74969	0.75959	0.9396
30.00	8.545	0.04455	3.51299	3.51299	2.75218	0.76081	0.9388
35.00	9.315	0.04857	3.51701	3.51718	2.75467	0.76251	0.9360
40.00	10.135	0.05284	3.52128	3.52162	2.75717	0.76445	0.9336
44.00	10.905	0.05686	3.52530	3.52577	2.75917	0.76660	0.9310
45.00	11.220	0.05850	3.52694	3.52745	2.75966	0.76779	0.9296
46.00	12.055	0.06285	3.53129	3.53183	2.76015	0.77168	0.9249
48.00	22.050	0.11497	3.58341	3.58403	2.76115	0.82288	0.8673

Sample 2.

V_{30}^{o} —   4.65926 c.c.

A   —   0.003422 sq. cm.

w   —   0.4561 gm.

W   —   56.3663 gm.

t	h	hA	V_{30}^{h}	V_{t}^{h}	V_{t}	v_{t}	D_{t}
35.00	0.345	0.00118	4.66044	4.66066	4.17235	0.48831	0.9340
40.00	1.275	0.00436	4.66362	4.66409	4.17613	0.48796	0.9347
42.00	2.190	0.00749	4.66675	4.66729	4.17802	0.48927	0.9322
45.00	2.940	0.01006	4.66932	4.66999	4.17990	0.49009	0.9306
46.00	4.720	0.01615	4.67541	4.67613	4.18063	0.49550	0.9205
46.60	5.370	0.01838	4.67764	4.67839	4.18111	0.49728	0.9172
46.80	5.805	0.01986	4.67912	4.67988	4.18127	0.49861	0.9147
47.10	6.040	0.02067	4.67993	4.68070	4.18149	0.49921	0.9136
47.20	8.705	0.02979	4.68905	4.68982	4.18157	0.50825	0.8974
47.50	9.350	0.03200	4.69126	4.69205	4.18180	0.51025	0.8939
47.60	9.485	0.03246	4.69172	4.69251	4.18188	0.51063	0.8932
47.80	13.120	0.04490	4.70416	4.70497	4.18203	0.52294	0.8722
48.00	14.200	0.04859	4.70785	4.70867	4.18217	0.52650	0.8663
48.30	14.350	0.04911	4.70837	4.70920	4.18240	0.52680	0.8658
49.00	14.665	0.05018	4.70944	4.71030	4.18292	0.52738	0.8648
50.00	15.165	0.05189	4.71215	4.71306	4.18367	0.52939	0.8616
50.50	15.825	0.05415	4.71341	4.71434	4.18406	0.53028	0.8601
50.60	18.280	0.06255	4.72181	4.72275	4.18414	0.53861	0.8468
50.70	32.385	0.11082	4.77008	4.77103	4.18421	0.58682	0.7772
52.00	32.830	0.11234	4.77160	4.77261	4.18519	0.58742	0.7764
55.00	33.890	0.11597	4.77523	4.77638	4.18745	0.58893	0.7744

t	h	hA	v_{30}^h	v_t^h	v_t	v_t	D_t
60.00	35.630	0.12193	4.78119	4.78257	4.19122	0.59135	0.7713
65.00	37.385	0.12793	4.78719	4.78880	4.19500	0.59380	0.7681
70.00	39.110	0.13383	4.79309	4.79493	4.19878	0.59615	0.7651
75.00	40.835	0.13974	4.79900	4.80107	4.20256	0.59851	0.7621
With Additional Mercury W - 56.9624 gm.							
5.00	5.750	0.01968	4.67894	4.67782	4.19363	0.48419	0.9420
10.00	6.960	0.02383	4.68309	4.68219	4.19744	0.48475	0.9409
15.00	8.190	0.02803	4.68729	4.68662	4.20125	0.48537	0.9397
20.00	9.205	0.03150	4.69076	4.69031	4.20506	0.48525	0.9399
25.00	10.460	0.03579	4.69505	4.69482	4.20887	0.48595	0.9386
30.00	11.735	0.04016	4.69942	4.69942	4.21268	0.48674	0.9370
35.00	13.030	0.04459	4.70385	4.70408	4.21649	0.48759	0.9354
40.00	14.385	0.04923	4.70849	4.70894	4.22031	0.48863	0.9334
44.00	15.560	0.05325	4.71251	4.71314	4.22336	0.48978	0.9312
45.00	15.925	0.05450	4.71376	4.71444	4.22412	0.49032	0.9302
46.00	16.560	0.05667	4.71593	4.71667	4.22488	0.49179	0.9274
48.00	27.150	0.09291	4.75217	4.75299	4.22641	0.52658	0.8662

(3) The density-temperature curves have been plotted for the range 0° to 80°C. , for the two samples. (Plate I at the end.) The density at 51.1°C., 0.7785 gm./c.c., obtained with Sample 1, has been found to correspond very well with the value found in Beilstein,[11] viz., 0.7786 gm./c.c. The low values found for Sample 2 are probably due to an error in the calibration of the dilatometer.

(4) The melting point of tetracosane has been found to be 50.7°C. using two methods. The value is lower than those found in the literature by 0.3° - [11] Beilstein, (loc. cit.)

0.3^o to 0.8^o, but is ingeneral agreement with Piper's results.[12]

(5) The transition points of tetracosane, as indicated by definite breaks in the density curves, have been found to occur at 47.9^oC. and $50.6+^o$C.. At these temperatures definite changes take place in the crystalline structure. The opaque form stable at room temperature is converted completely intohthertranslucent form at the lower transition point, while at the higher transition point, the translucent form is converted into a second opaque form, which is stable only within a few hundredths of a degree. Immediately above this second transition temperature, the hydrocarbon melts.

All the reactions were found to be reversible at the transition points, or more correctly, transition regions. It was found, however, that the metamorphosis from the translucent into the opaque form required many days, and perhaps weeks, before the transformation was complete. The change from the opaque into the translucent form did not require more than a few hours, before equilibrium was established. At the second transition point, equilibrium was reached in a few hours whether approached from below or above it. It was not possible to obtain a reading right at this point, because of the limitations of the thermostat.

(6) From the density-temperature curves, it can be seen that the curve for Sample 2 has a steeper slope at the first transition point than that for Sample 1. This shows that repeated fractional recrystallizations will purify a hydrocarbon, confirming the results obtained by Morris[13] with his work on dotriacontane.

[12]Piper et al, (loc. cit. p.2081).
[13]Morris, (loc. cit.).

IV. TREATMENT OF RESULTS.

(1) From the density-temperature curves, it may be seen that no sudden change takes place at 40° - 41°C., at which temperature Müller[14] observed a definite expansion in the cross-sectional area of the unit molecular crystal of tetracosane. From this fact, it may be inferred that changes in cross-section of the crystal have little or no effect on its density.

(2) The A and B forms of the 001 spacings have been found by Müller and Savile[15] to be 32.5 Å and 30.4 Å, respectively, for tetracosane. The ratio of the B to the A spacing is then 0.935. Now, if the density (0.8676) at the first transition point, 47.9°C., is divided by the estimated density (0.927) at the same temperature found by extrapolating the low temperature part of the curve, the ratio is found to be 0.935 again. It may therefor be inferred that the B form corresponds to the opaque form of tetracosane which is stable at low temperatures, and the A form corresponds to the translucent form. One may also say that the change in density at the transition point is due wholly to the change in molecular tilt.

If one appliesthe same calculations to the density curves of dotriacontane obtained by Morris[16] the ratio of the densities is found to be 0.8770 / 0.934 , i.e. 0.939. This shows that the opaque form of this hydrocarbon is of the B type as in the case of tetracosane. One wonders why Piper and his associates could not obtain B spacing measurements for dotriacontane.[17]

If it is assumed that the A form is the translucent and vertical type of crystal, then the ratio B:A corresponds to the sine of the angle of

[14]Müller, (loc. cit.)
[15]Müller and Savile, Proc. Roy. Soc. Lond., 127A, 417 (1930)
[16]Morris, (loc. cit.)
[17]Piper et al, (loc. cit.)
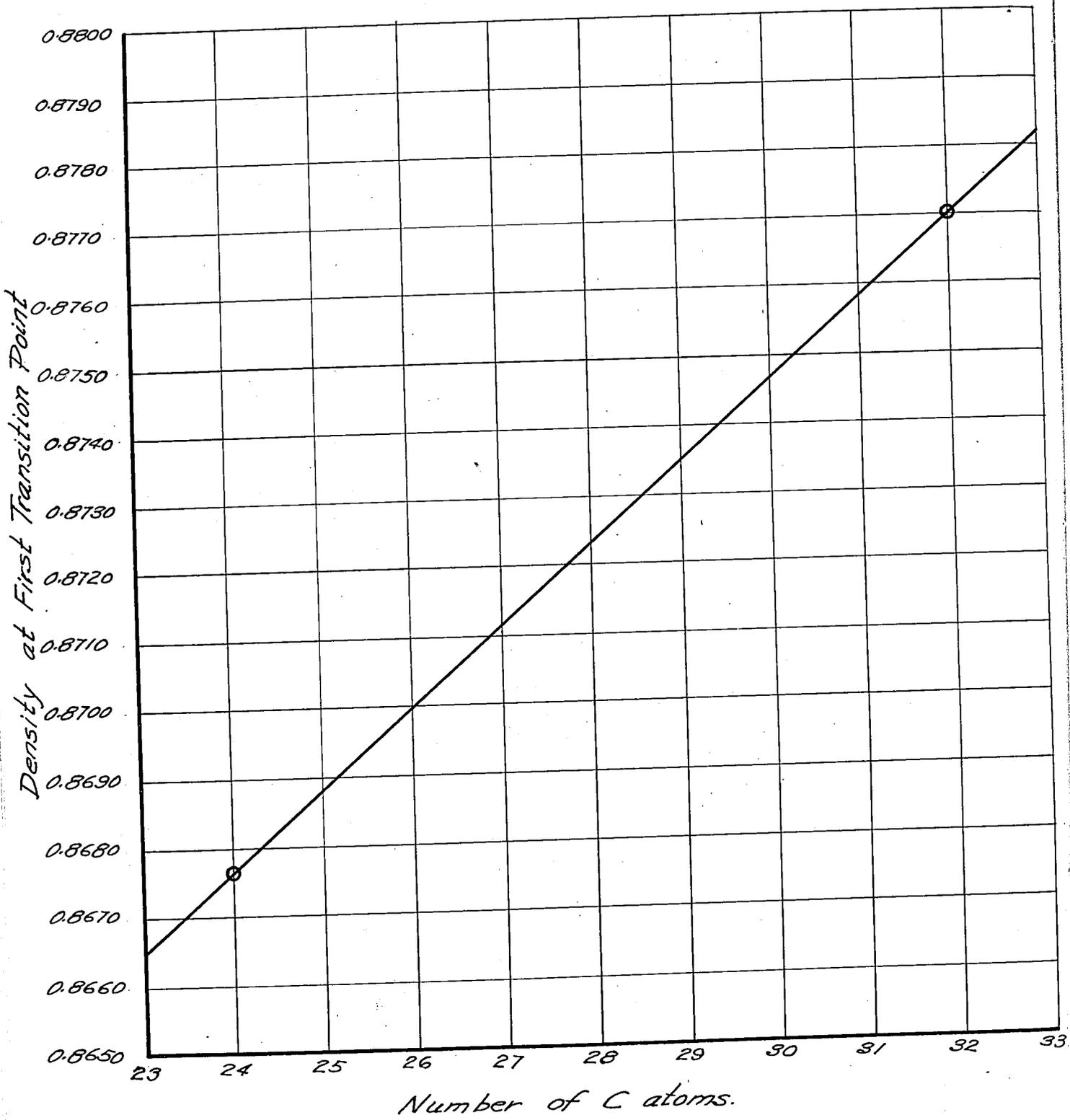
Fig. 3 (To face page 16)

molecular tilt, which angle when calculated for the case of tetracosane comes to 69.5°.

(3) Since the A spacing is a linear function of the number of carbon atoms in the hydrocarbon molecule,[18] it is perhaps safe to infer that the density at the first transition point is also a similar function. Using the values obtained with tetracosane and dotriacontane, a graph has been plotted for C_{23} to C_{33} paraffins. (Fig. 3.) The predicted densities are tabulated below:

<div align="center">TABLE III</div>

No. of C atoms	Density at First Trans. Pt.
23	0.8664 gm./c.c.
25	0.8688
26	0.8700
27	0.8711
28	0.8723
29	0.8734
30	0.8746
31	0.8758
33	0.8782

(4) From the density-temperature curve for Sample 1, the following density equation was established for the liquid line:

$$D_t = 0.7788 - 0.00064 (t - 50.7)$$

where D_t is the density at temperature $t°$ C.

Applying this equation to three densities found in Beilstein,[19] the values corresponded very well. They are tabulated below:

[18] Piper et al, (loc. cit. p.2080)
[19] Beilstein, (loc. cit.)

TABLE IV

| Temperature | Density | |
	Beilstein	Calculated
51.1° C.	0.7786	0.7785
76.0°	0.7628	0.7626
98.9°	0.7481	0.7480

From the same curve the coefficient of cubical expansion of the liquid hydrocarbon was determined. Its value was found to be 0.0008411 c.c./c.c./ °C. The specific volume equation for the liquid tetracosane is then:

$$V_t = 1.2840 (1 + 0.0008411 (t-50.7))$$

where t is any temperature above 50.7°C.

The liquid line was found to be exactly parallel to that for dotriacontane, showing that all liquid paraffins have the same coefficient of cubical expansion.

(5) For the solid part of the curve, it was seen to require a complicated form of equation. Due to lack of time, its derivation was not carried out. The curve was, however, seen to be quite parallel to that of dotriacontane. A further observation indicated that both hydrocarbons in the opaque solid form have practically the same density.

V. SUMMARY.

(1) The density-temperature curves for two samples of n-tetracosane have been determined and plotted for the range 0° to $80^\circ C$.

(2) Two transition points have been determined.

(3) An equation has been developed for the density above the melting point.

(4) The coefficient of cubical expansion of the liquid hydrocarbon has been determined.

(5) An attempt has been made to correlate the results obtained with tetracosane to those of dotriacontane in order to generalize some properties.

(6) The density has been found to be independent of changes in cross-sectional area of the crystals, but is affected greatly by the molecular tilt.

VI. CONCLUSION.

The author wishes to take this opportunity to express his appreciation to Dr. W.F. Seyer for his kind interest in this work. Without his valuable suggestions and assistance this work would not have been possible.

VII. <u>BIBLIOGRAPHY</u>.

(1) Beilstein: Handbuch der organischen Chemie, Vol. I, p. 107 (1893)

(2) Godard, H.P., "Solubility of Tetracosane in Propane, Butane and Pentane," Thesis submitted for M.A.Sc. Degree, U.B.C., April, 1937.

(3) Krafft, Berichte, 19, 2219 (1886).

(4) Morris, W.M., "Density and Transition Points of Dotriacontane (Dicetyl)," Thesis submitted for M.A.Sc. Degree, U.B.C., April, 1938.

(5) Müller, A., Proceedings of the Royal Society, London, 130 A, 514 (1932).

(6) Müller, A and Savile, Proceedings of the Royal Society, London, 127 A, 417 (1930).

(7) Piper, S.H., Chibnall, A.C., Hopkins, S.J., Pollard, A., Smith, J.A.B., and Williams, E.F., Biochemical Journal, 25, 2072-2094, (1931).

(8) Hildebrand and Wachter, Journal of the American Chemical Society, 51, 2487 (1929).
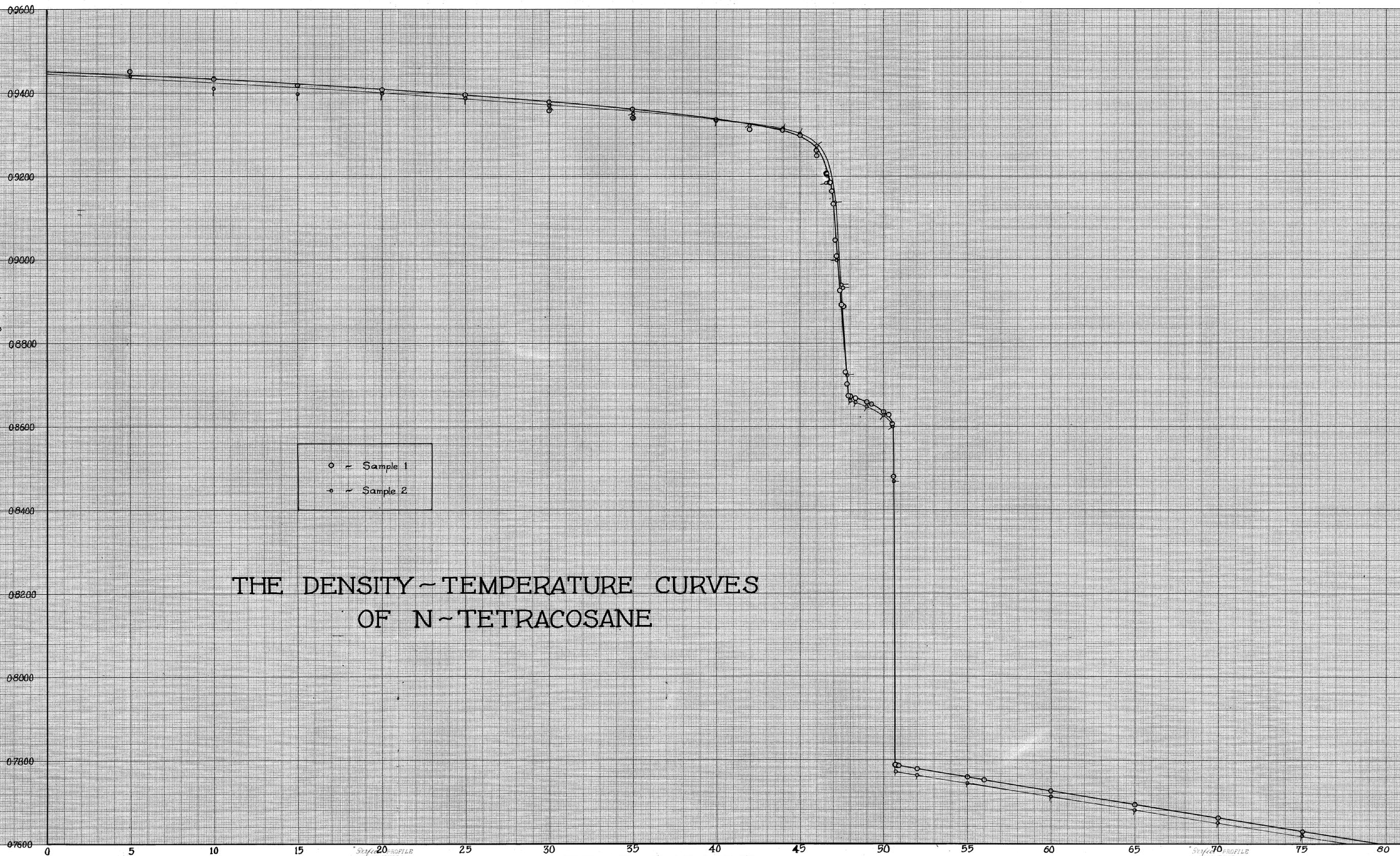
THE DENSITY~TEMPERATURE CURVES
OF N~TETRACOSANE

DENSITY ~ gms/cc.

TEMPERATURE ~ degrees C.