THE SOLIDIFICATION POINTS OF HEXAMETHYLENEIMINE

by

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A Thesis Submitted in Partial Fulfilment of the
Requirements for the Degree of
Master of Applied Science
in the Department
of
Chemical Engineering

The University of British Columbia
September, 1946

Accepted on behalf of the Department
of Chemistry

Head of the Dept. of Chemistry

PREFACE

I wish to acknowledge the valuable assistance and helpful suggestions given by Dr. W. F. Soyer of the Department of Chemistry. I am also grateful to H. Scroce of the Ethyl Corporation who was very co-operative, and supplied the sample of Hexamethylethane.

F. Campbell William,
September, 1946

THE TRANSITION FORMS OF HEXAMETHYLETHANE

This investigation and others carried out in the same laboratory were done for two reasons. Theoretically this work adds to the accumulation of scientific data. Also it is of interest from an engineering point of view because the efficiency of design work is directly proportional to the number of unknown factors that can be eliminated. In the last few years a great deal of research has been done by the petroleum industry on the determination of the physical and chemical properties of the hydrocarbons present in fuels. In automotive fuels it has been found that certain branched straight chain hydrocarbons are essential in producing high grade gasoline, because of their temperature stability and power. Because hexamethylethane (2,2,3,3 tetramethylbutane) has been found in fuels, it is important to know its physical properties.

Hexamethylethane has long been of interest to chemists because of its unusually branched and symmetrical structure and the effect of this structure on its physical properties. Hexamethylethane is a solid at ordinary temperatures, it melts at 100.6° C and boils at 106.6° C.

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LIST OF ILLUSTRATIONS

The following vapour pressures[2] have been determined:

	10.37 C	9.8 mm Hg
	20.90	17.4
	30.93	40.1
	79.96	300.6
	95.00	531.9
	98.98	613.2
	100.00	635.6
solid	100.03	636.6
liquid	101.05	657.4
	106.07	757.2

From these figures it can be seen that the hydrocarbon must be handled carefully and that if left in a container that is unsealed it will vapourize into the atmosphere very rapidly. It can also be seen that if the hydrocarbon is not pure that the combined vapour pressure of the impurity and the hydrocarbon in the region of 99 C will be greater than that of atmospheric pressure. The heat of combustion at constant pressure was found to be very close to that of iso-octane, being 1301.3 K-cal. /mol[3] and also the octane number[3] is 103 which makes it useful in gasoline blending. Because hexamethylethane is the simplest compound containing two "neo" carbon atoms, it is of interest, theoretically, in the field of intra-molecular rearrangements.[4,5]

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1. Doss, Physical Constants of Principal Hydrocarbons 1943
2. Calingaert, Soroos, Hnizda, and Shapiro, J. Am. Chem. Soc. 66, 1389,1944.
3. Day and Pease, J. Am. Chem. Soc., 58, 153, 1936.
4. Whitmore, Barker, and Fleenbook, J. Am. Chem. Soc., 54, 3274, 1932.
5. Whitmore, J. Am. Chem. Soc., 54, 3274, 1932.

Investigations have shown that when the quaternary grouping is symmetrical, as is the case with this compound, there is a peculiar effect of restricting the liquid range combined with a large increase in the density of the compound compared to the normal isomer. The following data is given by Morgan, Carter, and Duck.[6]

	M.P.	B.P.
	°C	°C
n pentane	-130.8	36.3
2,2 diethyl propane	- 20.0	9.5
n nonane	- 51.0	150.5
3,3 diethyl pentane	- 41.0	139.2
n octane	- 57.4	124.7
hexamethylethane (double quaternary grouping)	+101.6	106.6

This compound melts above 100 °C or 150 degrees above the n ormal isomer and as high as hexacontane ($C_{60}H_{122}$) while retaining the volatility to be expected of a hydrocarbon of its low molecular weight.

When determining the thermal data on hexamethylethane Parks, Huffman, and Thomas[7] found a transition point between two crystalline forms at -135 °C and measured the heat of transition (4.20 cals/gm). From cooling curve data obtained from research done at the Ethyl Corporation Research Laboratory, another transition point was found to exist near the melting point. Because the change in crystal structure in normal paraffins is accompanied by a change in density,

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6. Morgan, Carter, Duck 127, 1257, 1925 J. Am. Chem. Soc.
7. Parks, Huffman, and Thomas J. Am. Chem. Soc. 52, 1032, 1930

it was decided to investigate the density and transition points of hexamethylethane by the dilatometer method similar to that used by W. F. Seyer, R. F. Patterson and J. L. Keays.[8]

GENERAL THEORY ON CRYSTAL FORMS

It has been found by X-ray studies by Saville,[9] Muller,[10] Piper,[11] and others that many members of the paraffin series along with other long chain hydrocarbones exist in several enantiotropic forms. These studies have shown that at the point of transition from one crystalline form to another there is only a very slight change in the basal area of the crystals but a very large change in the 001 lattice spacings, resulting in a change in the density. Because of this fact, density changes with temperature can be used to measure the transition points and the relationship between the density and the possible crystalline forms.

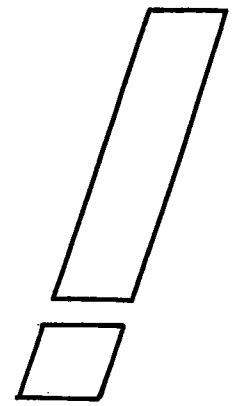
There appears to be general agreement that the aliphatic hydrocarbons exist in at least three crystalline forms.

A. Form

8. Seyer, Patterson, Keays, J.Am Chem. Soc. 66,179,1944
9. Saville, Chem.Soc. 127,591,1925
10. Müller, Proc. Roy Soc (London) 514,1932.
11. Piper et al, Biochem. J. 25,2072,1931

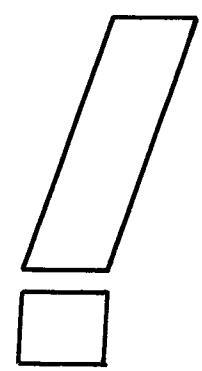
The chain axis is vertical to the 001 plane and the planar spacings are a direct measure of the length of the molecules. Even members of C18 or more carbon atoms and odd members of C11 or more carbon atoms show this form near the melting point.

B Form



A lower form of symmetry-- the crystals are not rectangular in cross section and the chains may be inclined at a constant relative to the base. Even number paraffins up to C24, at normal temperatures crystallize with the chain axis inclined at a constant angle to the 001 plane. Muller[10] found that the 001 spacings of this modification are shorter than the spacings for the A form. As an example, for C26 the spacing for the A form is 34.95 A°. while for the B form it is 31 A°.

C Form



This form has a rectangular cross section with the chain tilted relative to the base of the crystals.

MATERIAL (Cont'd)

The hexamethylethane sample was supplied by the Chemical Research Laboratory of the Ethyl Corporation. The sample was prepared as described by Calingaert, Soroos, Hnizda, and Shapiro.[2] It was prepared by the condensation of 2,3,3 trimethyl 2 chlorobutane with methyl magnesium chloride and purified by fractional distillation in a specially designed pressure still.

Freezing and melting curves are obtained on the best fractions. From this data the purity of the products is calculated to be 99.90 ± .04 mol per cent.

Apparatus:

The constant temperature bath used was similar to baths used in this laboratory for other density research in straight chain hydrocarbons. The bath consisted of a large pyrex glass container insulated with approximately 3 inches of rock wool. The bath contained a double bladed stirrer, two heaters, and a temperature control. One heater was used to keep the bath just under the required temperature and the second smaller heater was connected to the temperature control for quick and fine temperature changes.

Temperature Control:

Up to 70° C a mercury control was used. However, at higher temperature it was found that there was a lag in

Temperature Control (Cont'd)

in control and that the best control to be obtained was $\frac{1}{20}$ °C. For that reason temperature controls were made from liquids that boil near the temperature at which they were used. At the boiling point the liquid is in equilibrium with its vapour and a slight change in the temperature gives a large change in the volume of the vapour. This change gives a very accurate control of the temperature. A different liquid was used every 1° and with these controls, temperatures were regulated to ± 0.01 °C.

Because the temperature control was so important especially near the transition points and melting points the apparatus was carefully watched at all times, for a change in line voltage affected the heaters considerably. Some of the points did not come to equilibrium for more than 72 hrs. therefore it had to be arranged for constant observation.

Experimental Procedure:

Dilatometer

The dilatometer method is one of the most accurate means of determining the density of compounds. An accurately weighed sample is placed in the bulb and is covered by distilling mercury into it under vacuum. The change in the height of the level of the mercury in the capillary gives the change in volume of the substance over the temperature recorded. Since the weight and volume of the mercury are known and the weight of the substance, the density of the substance can be

calculated. Corrections are made for the expansion of glass and the buoyancy of the air.

The capillary tube was selected from a piece of small bore capillary tubing of uniform diameter. The diameter was calibrated by measuring the length of a weighed amount of mercury.

Heavy pyrex tubing was used to blow the glass bulb. The tubing was sealed to the bulb and mercury distilled into the bulb under a pressure of 1×10^{-4} mm.

Filling the Bulb.

Difficulty was encountered in filling the bulb with the hydrocarbon. The high vapour pressure and the narrow liquid range of the compound made it difficult to handle. To prevent the formation of crystals on the capillary wall of the bulb the following method was used. The ampoule of hydrocarbon, the bulb, and funnel were sealed in the glass tube. The tube was evacuated and filled with hydrogen at a pressure of 25#/in.^{2} The sides of the container were gradually heated and the hexamethylethane flowed through the funnel into the bulb.

Two samples of hydrocarbon were received from The Ethyl Corporation. With the first sample R.B.Bennett[12] plotted most of the density curve but did not complete the curve of the less dense phase. With the second sample the same procedure was followed but it was found for four different trials that at 98°C the vapour pressure of the hydrocarbon forced the

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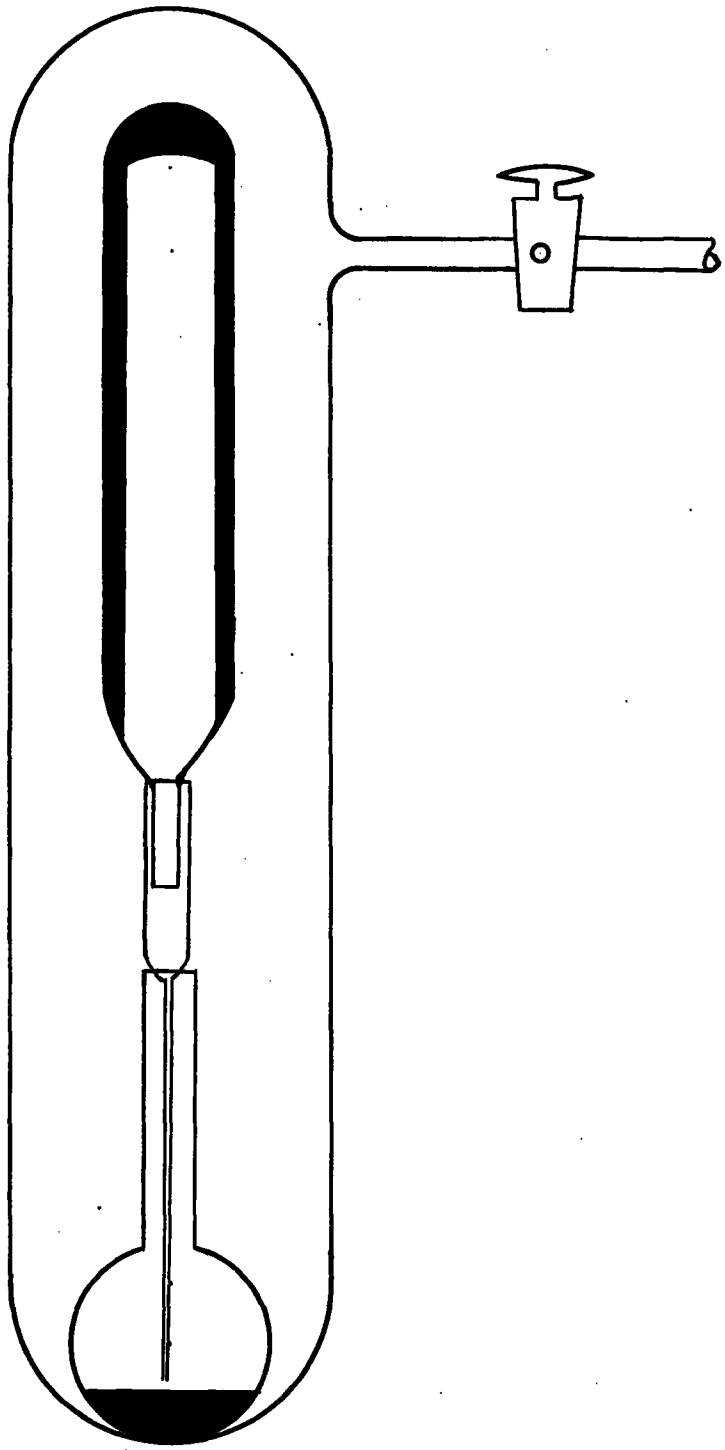
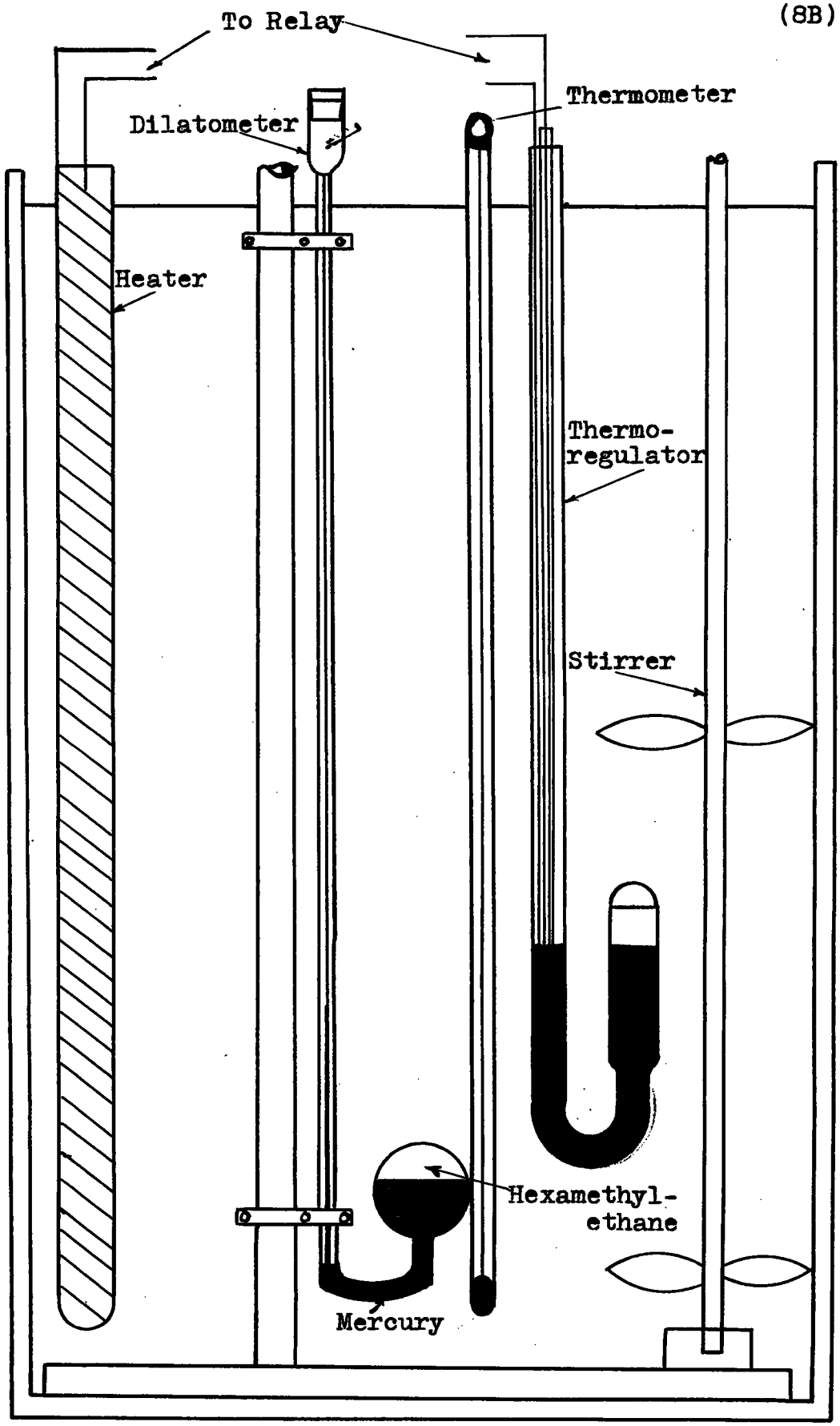
12. R.B.Bennett, Master's Thesis, The University of B.C.,1945.



Filling the Bulb
Fig. 1



Constant Temperature Bath
Fig. 2

mercury out of the dilatometer. On checking the vapour pressures as observed by Calingaert, Soroos, Hnizda, and Shapiro[2], it was decided that some of the solvent used in the preparation of hexamethylethane must still be present in the hydrocarbon. To overcome this a bulb was filled with the hydrocarbon and joined to the dilatometer capillary tube. The dilatometer was then connected to a system which was evacuated by a Cenco vacuum pump and by a mercury vacuum pump until the pressure was 1×10^{-4}. The hydrocarbon was then melted and vapourized but immediately solidified again in the U of the dilatometer with dry ice. When the hydrocarbon was heated the highly volatile solvents were vapourized and pulled off by the vacuum pumps. The pressure in the system was raised to atmospheric and the hydrocarbon distilled back into the bulb by placing dry ice around the bulb and gently heating the hydrocarbon in the U of the dilatometer. This sample gave the true melting point.

Measurements

The only experimental measurements necessary were the heights of mercury in the capillary and the corresponding temperature ofthe bath. The temperature was measured by a thermometer calibrated against a platinum resistance thermometer. The capillary heights were measured by a cathetometer graduated in 0.001 mm. The capillary heights were plotted as the readings were taken so that any sudden or large change in density could be detected . In this way

it was apparent where to take readings over a small change in temperature to determine the exact transition points.

It was found that at the lower temperatures equilibrium was reached in about 15 minutes. After 80°C it took about 30 minutes to rech equilibrium and near the transition points it required 7½ hrs. before the capillary heights came to a constant reading.

Calibration of the Capillary Tube.

To determine the cross section of the capillary tube of the dilatometer a known weight of mercury was placed in the capillary and the length of the mercury measured at intervals along the capillary. These results were later checked when the bulb was filled with mercury and the expansion measured between two temperatures. For the first method a value of 0.00393 sq.cm. was determined and for this second method a value of 0.00396 sq.cm.

Sample Calculation.

Mass of Hg = 149.2362 gms

Vol. at 84.80°C. = 11.14663 cc

Vol. at 43.94°C. = 11.06362 cc

Difference = 0.08301 cc

Correction for the expansion of glass

= 40.86 (11.06362)(0.0000096)

= 0.00434 cc

Net expansion of Hg = 0.07867 cc.

Difference in Hg levels = 19.853 cms.

Area of cross section = $\frac{0.07867}{19.853}$ = 0.00396 sq.cms.

Calculation of Densities:

Symbols

t = temperature at which readings were taken in $^{\circ}C$

h = height of Hg above zero mark

A = cross section area of capillary

$V29^{\circ}$ = Volume of the bulb to the zero mark at $29^{\circ}C$

$V29^{h}$ = Total volume to height h at $29^{\circ}C$
$= V29^{\circ} + hA$

V_t^h = Total volume to height h at $t^{\circ}C$

$= V29^{h} + V29^{h}(t-29)(a)$ where $a = 0.0000096 cc/cc/^{\circ}C$

W = Total mass of mercury

V_t = Volume of mercury at $t^{\circ}C$

w = Mass of hydrocarbon in bulb

v_t = Volume of hydrocarbon in bulb at $t^{\circ}C$

$= V_t^h - V_t$

D_t = Density of hydrocarbon at $t^{\circ}C$

$= \frac{w}{v_t}$

Example of calculations:

$h = 18.359$ cms.

$t = 80.96\ ^{\circ}C$

$A = 0.00396$ sq. cm.

$hA = 18.359(0.00396) = 0.0727$ cc.

$V29^{\circ} = 4.8600$ cc.

$V29^{h} = 4.8600 + 0.0727 = 4.9327$ cc.

$V_t^h = 4.9327 + 4.9327(80.96 - 29)(0.0000096)$

$= 4.9352$ cc.

Example of calculations: (Cont'd)

$W = 53.0967$ gms.

$V_t = 53.0967(0.0746393)$ cc

$= 3.9631$ cc

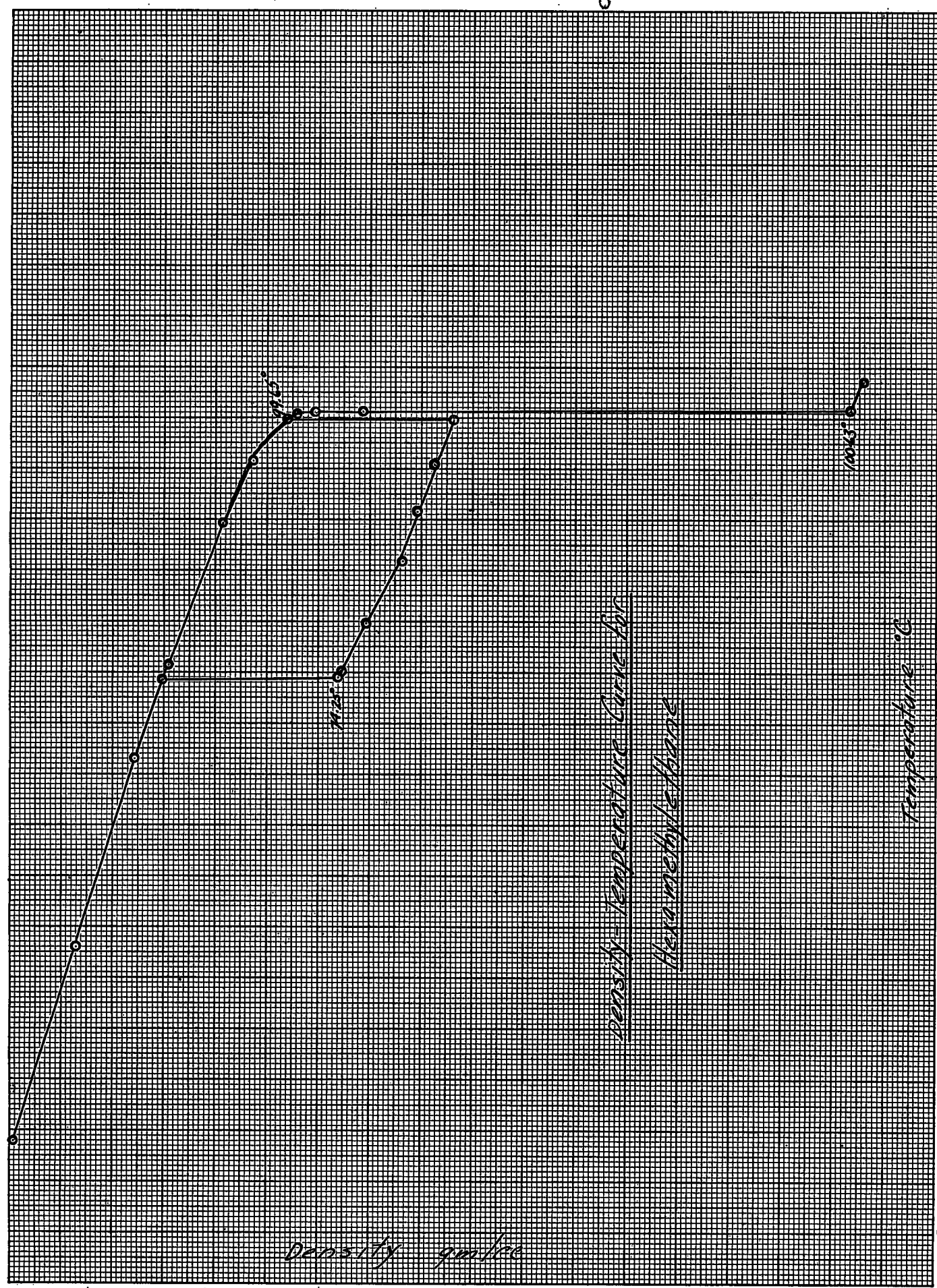
$v_t = V_t^h - V_t = 4.9352 - 3.9631 = 0.9721$ cc

$w = 0.7633$ gm.

$D_t = \frac{w}{v_t} = \frac{0.7633}{0.9721} = 0.7852$ gm/cc

Results.

Temp.__°C	Density	Temp.__°C	Density
20.00	0.8230 gm/cc	88.50	0.7792 gm/cc
29.00	0.8196	89.74	0.7782
48.20	0.8070	91.82	0.7767
52.75	0.8047	93.24	0.7751
62.25	0.7986	95.89	0.7725
66.50	0.7955	97.10	0.7708
70.20	0.7928	98.35	0.7690
71.56	0.7919	99.45	0.7683
73.00	0.7913	99.96	0.7652
74.42	0.7900	100.10	0.7641
75.85	0.7890	100.34	0.7601
76.23	0.7887	100.52	0.7538
77.20	0.7880	100.56	0.7519
78.46	0.7871	100.63	melting point
79.10	0.7866	100.71	0.6568
79.55	0.7863	100.84	0.6566
80.10	0.7859	101.18	0.6563
80.96	0.7852	101.92	0.6557
82.00	0.7844	102.28	0.6553
83.15	0.7836	102.58	0.6551
84.20	0.7829	102.81	0.6549
85.78	0.7816	103.50	0.6542
86.02	0.7810		
87.70	0.7797		


Density-temperature curve for
Benzene/Ethanol
Density gm/cc
Temperature °C
0.82
0.80
0.78
0.76
0.74
0.72
0.70
0.68
0.66
0.64
20
30
40
50
60
70
80
90
100
110
94.5°
77.3°
103.3°

Descending Temperatures Only

Temp	Density	Temp	Density
99.65	0.7334	86.35	0.7436
98.70	0.7343	85.71	0.7439
97.75	0.7353	84.09	0.7456
97.12	0.7358	83.31	0.7465
96.56	0.7361	82.91	0.7469
95.43	0.7372	81.75	0.7480
94.61	0.7379	79.63	0.7502
93.52	0.7388	77.64	0.7519
92.75	0.7201	75.96	0.7541
91.57	0.7398	75.62	0.7552
90.73	0.7406	74.85	0.7564
89.67	0.7412	74.30	0.7658
88.37	0.7421	74.25	0.7902

Results:

The main result of the research is the density temperature curve. This curve is a plot of the densities, calculated from the capillary heights, against the temperature. It shows a hysteresis, where the density follows the higher curve on heating and the lower curve on cooling. The first transition point on cooling was found to be 99.65 °C. and the second transition point was found to be 74.25 °C. At 74.25 °C. the curve breaks upward and again joins the curve obtained for the densities when the hydrocarbon was heated from 20 to 100.63 °C. On further cooling, from 74.25 to 30 °C. the curve follows the original density line. The melting point was found to be 100.63 °C.

(2) The density at 30 °C. was found to be 0.8830 in agreement with earlier investigations.

(3) For the liquid the specific volume equation was found to be $V_t = 1.3226(1 + .001351(t - 100.63))$ where the coefficient of expansion is given by 0.001351 cc/cc/ °C.

Results (Cont'd)

(4) The density for the liquid is given by

$$D_t = 0.6567 - 0.00089(t - 100.55)$$

Discussion of Results:

The temperatures were read accurately to ± 0.01° C and the capillary heights were read accurately to ± 0.003 cm. The weight of the mercury and the weight of the hydrocarbon are accurate to ± 0.0001 gms. These values warrant an accuracy of four places of decimals in the values of the density. However, depending on whether the cross section of the capillary tube was taken as 0.00373 sq. cms as observed by the first method or 0.00396 sq cms as observed by the second method, a discrepancy of 5 occurs in the fourth figure after the decimal. Therefore we may conclude that the densities as given are accurate to the fourth figure ± 0.0005.

If the density curve for the liquid is extrapolated to 20° C it agrees very well with the results of Calingaert.[13] The value found here is 0.7203 gm/cc compared to the value of 0.7219 gm/cc observed by Calingaert. In the density equation for the liquid the coefficient is 0.00089 which is in agreement with 0.00093, the average coefficient for branched chain hydrocarbons, as found by Calingaert.[13] In this laboratory Yatabe[14] found, for normal paraffins,

13) Calingaert, Beatty, Huber, Thomas, Ind. Eng. Chem 33, 103, 1941

14) Yatabe, Master's thesis, University of British Columbia 1930.

a coefficient of 0.00064. It is to be expected that the value for hexamethylethane would be larger, because for normal hydrocarbons hexagonal packing was assumed, but for hexamethylethane we may assume body-centered packing of roughly spherical mols as interpreted by C.D.West.[15]

At the melting point the percentage decrease in density is 12.5%, or the density of the liquid is 87.5% of the density of the solid immediately before melting. On cooling the liquid it first forms an opaque solid. This would suggest a random distribution of small crystals which prevent light from passing through. On further cooling to 99.65°C, the first transition point, a less dense packing occurs for the decrease in density is 4.5%. It is interesting to note that at the second transition point, 74.25°C, the percentage increase is 4.5%. From this we may assume that the solid crystallizes in two forms, "a" and "b". On heating from room temperature it exists in form "a" until it melts. However, on cooling it transforms to the less dense form "b" at 99.65°C and exists as form "b" until 74.25°C. At 74.25°C the hydrocarbon changes back to the more dense form "a". C.D.West[15] determined that hexamethylethane was plastic and isotropic and sublimed into well-formed dodecahedrons. Therefore we may assume that the crystals of hexamethylethane in the more dense form are dodecahedrons.

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15. C.D.West, Zeitchriste fur Kristalographie, 88, 195, 1934.

APPENDIX

Specific Volume of Mercury from 0°C to 105°C.

For the specific volume of mercury the following values were used:

Temp.	Spec. Vol.	Temp.	Spec. Vol.
20.0	0.0738233	63.0	0.0744246
21.0	8367	64.0	4381
22.0	8501	65.0	4516
23.0	8635	66.0	4650
24.0	8765	67.0	4785
25.0	8902	68.0	4850
26.0	9036	69.0	4885
27.0	9170	70.0	4919
28.0	9304	71.0	5053
29.0	9437	72.0	5188
30.0	9571	73.0	5322
31.0	9705	74.0	5457
32.0	9839	75.0	5587
33.0	9973	76.0	5733
34.0	0.0740107	77.0	5868
35.0	0241	78.0	5996
36.0	0374	79.0	6130
37.0	0508	80.0	6264
38.0	0642	81.0	6399
39.0	0776	82.0	6535
40.0	0891	83.0	6670
41.0	1024	84.0	6804
42.0	1158	85.0	6939
43.0	1823	86.0	7074
44.0	1426	87.0	7209
45.0	1560	88.0	7344
46.0	1695	89.0	7479
47.0	1829	90.0	7614
48.0	1963	91.0	7749
49.0	2097	92.0	7884
50.0	2231	93.0	8019
51.0	2365	94.0	8154
52.0	2500	95.0	8288
53.0	2634	96.0	8423
54.0	2768	97.0	8558
55.0	2903	98.0	8693
56.0	3037	99.0	8828
57.0	3171	100.0	8963
58.0	3305	101.0	9008
59.0	3440	102.0	9143
60.0	3843	103.0	9278
61.0	3978	104.0	9413
62.0	4112	105.0	9548