

THE DENSITY AND COEFFICIENT OF EXPANSION OF  
HEXAMETHYLETHANE

by

Reginald B. Bennett

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*Accepted on behalf of the  
Department of Chemistry.*

*Head of the Dept. of Chemistry.*

## PREFACE

The ultimate purpose of this research was to collect data on the density and coefficient of expansion of a branched straight-chain hydrocarbon, hexamethylethane. During the past several years similar data has been obtained in this laboratory on several normal straight-chain hydrocarbons by William Morris,<sup>12</sup> Eiji Yatabe,<sup>25</sup> Ralph Patterson,<sup>17</sup> and John Keays.<sup>7</sup> Since the normal paraffins (even numbered) have been examined fairly completely between C<sub>16</sub> and C<sub>34</sub> it was decided to investigate a branched paraffin. It should be pointed out that the density of the compound has not been examined completely between 70°C and 99°C.

Care has been taken to describe all phases of the work undertaken as completely as possible although the method of measuring the densities was exactly the same as that used in previous work here. This should serve as an aid to those who fill in the blank region existing in the density curve.

I wish to acknowledge the valuable assistance and helpful suggestions given by Dr. W. F. Seyer of the Department of Chemistry throughout the course of the work. I am also indebted to H. Soroos of the Ethyl Corporation for the sample of hexamethylethane.

Reg. B. Bennett  
September, 1945

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THE DENSITY AND COEFFICIENT OF EXPANSION OF  
HEXAMETHYLETHANE.

During the past 20 years a great deal of research has been carried out by the petroleum industry, particularly on liquid fuels. Much of this work has been confined to the determination of the physical and chemical properties of the different hydrocarbons which are present. In the case of automotive fuels it has been found that the presence of certain branched straight-chain hydrocarbons is essential for the production of high grade gasolines because of their temperature stability and power. For this reason, hexamethylethane (2,2,3,3 tetramethylbutane) is of prime interest.

Data have been obtained for some of the physical properties of hexamethylethane. The heat of combustion at constant pressure was found to be very close to that of iso-octane, being 1301.3 K-cal./mole. The octane number of hexamethylethane is 103 which makes it useful for blending purposes. Although it is a solid at ordinary temperatures, hexamethylethane melts at 101.6°C and boils at 106.6°C. The following vapour pressures of the solid have been determined by E. Linder:

TABLE I

-10.3°C	1.33 mg Hg
- 5.0	2.08
- 0.3	3.55
6.0	5.80

Since hexamethylethane is the simplest compound containing two neo carbon atoms it is of particular interest, theoretically, in the field of intramolecular rearrangements.<sup>23,24</sup> 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 density of the compound. The following data is given by Morgan, Carter, and Duck:<sup>11</sup>

TABLE 2

	<u>M.P.</u>	<u>B.P.</u>
n-pentane	- 130.8	36.3 <sup>o</sup> C
2,2 diethyl propane	- 20	9.5
n-nonane	- 51	150.5
3,3 diethyl pentane	- 41	139.2
n-octane	- 57.4	124.7
hexamethylethane (double quaternary grouping)	+103	+106

The crystalline structure of hexamethylethane has been investigated by several men. C. West<sup>22</sup> found that the compound was plastic and isotropic forming dodecahedrons when sublimed. This may be interpreted on the basis of a body-centred packing of roughly spherical mols. Powder photography indicated body-centred crystals containing two molecules, similar to hexachlorethane. While determining thermal data on hexamethylethane Parks, Huffman, and Thomas<sup>15</sup> found a transition point between two crystalline forms at -125<sup>o</sup>C and measured the heat of transition (4.20 cal/gm). From cooling curve data obtained by the Ethyl Corporation another transition point was found to exist near the melting point. Since the variation in the crystalline structure of

normal paraffin hydrocarbons is known, in many cases, to be accompanied by a variation in the density, it was decided to investigate the density and transition points of the hexamethylethane by the dilatometer method and determine the coefficient of expansion.

#### CRYSTAL FORMS OF NORMAL PARAFFINS.

It has been shown by X-ray studies by Saville,<sup>20</sup> Müller,<sup>14,15</sup> Piper,<sup>16</sup> and others that many members of the paraffin series, along with other long-chain hydrocarbons, exist in several enantiotropic forms. It was also found that at the point of transition from one crystalline form to another there was 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 sharp change in the density. Because of this fact, density changes with temperature can be used to determine the transition temperature and the relationship between the density change and the crystalline form.

It has been shown by A. Müller<sup>14,15</sup> that the aliphatic hydrocarbons may exist in at least three crystalline forms:

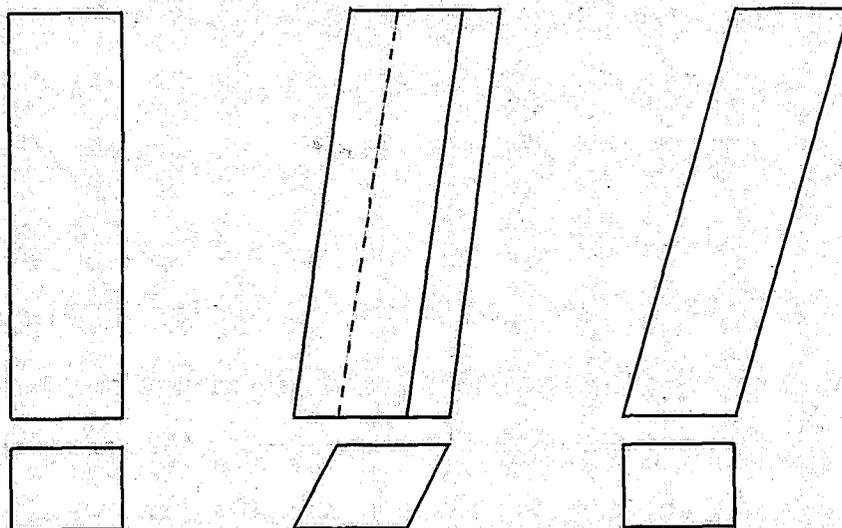
A. The normal form - the crystals are right rectangular prisms with the chain axis perpendicular to the base. In this form the planar spacings are a direct measure of the length of the molecules.

B. 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.

C. A form which has a rectangular cross-section with the chains tilted relative to the base of the crystals.

Figure 1.



The hydrocarbons with an even number of 18 or more carbon atoms and odd members of 11 or more carbon atoms exist in the A form near the melting point. This is a characteristic property of the even-numbered paraffins up to C<sub>44</sub>. Even numbered paraffins up to 24 atoms crystallize in the B modification at normal temperatures. Near the melting temperature the B crystals are converted to the A form but revert to the B form when cooled. Odd numbered chains of 9 or less carbon atoms also exist in the B form at normal temperatures. The paraffins with 26 or more carbon atoms crystallize, when pure, in the C modification, and show a higher transition temperature. In the case of n-tetratriacontane (34 carbon atoms) Piper<sup>16</sup> identified the crystals in the C form as rhombs of acute angle 73°.

Apparently odd number paraffins never take the C form, but Müller found single crystals in the A form with an acute angle of  $63^{\circ}$ . The paraffin with 26 carbon atoms is the only hydrocarbon that shows all three phases.

The members 18, 20, and 22 give a different density curve on heating than they do on cooling. Müller recorded this phenomenon from measurements of the length of the carbon chain. It was shown by Keays that the density-temperature characteristics of 20 and 22 were the same as 24, 26 etc., with decreasing temperatures and similar to the lower even-number members of the series with decreasing temperatures.

An investigation of the liquid state of several hydrocarbons by Keays showed that the density-temperature lines were straight and almost parallel. Since the lines are straight and have the same slope it has been concluded that the molecules are in a liquid crystalline state. From observations made by Müller it is believed that hexagonal packing occurs in this temperature region.

The crystalline structure of the normal paraffins has also been investigated by C. G. Gray by microscopic methods. He has shown that there are four crystalline forms.

1. The hexagonal system
2. The orthorhombic system
3. The monoclinic or triclinic system with the molecules tilted at an angle of  $73^{\circ}$  to the base of the crystal.

4. The monoclinic or triclinic system with two unequal side spacings but with the molecules tilted at an angle of  $61^{\circ}30'$  to the base of the crystal.

The ranges of the four modifications are as follows:

1. Odd paraffins from C 11 upwards; even from C 18 upwards.

2. Odd from C 11, even from C 18 upwards.

3. Odd from C 5 to C 9 inclusive, even from C 6 to C 22 inclusive.

4. Even only from C 24 to C 26 inclusive. This modification has been obtained only by crystallization from solvents. It has not been obtained by crystallization of melts or by transition from one of the other modifications.

It must be remembered that the crystalline forms given have been determined for the normal paraffins only. It still remains to be found whether or not the branched paraffins will also crystallize in the same forms. Since hexamethylethane is isotropic it is doubtful that the same crystalline forms are present.

#### EXPERIMENTAL PROCEDURE.

##### (1) Theory of the Dilatometer.

The dilatometer method is one of the most accurate means of determining the density of organic compounds. An accurately weighed sample of the substance is placed in a dilatometer and then mercury is distilled in

under a vacuum until the bulb is filled. Density changes in the compound at different temperatures are indicated by changes in the height of the mercury column in the capillary tube of the dilatometer. Since the volume and weight of the mercury is known along with the weight of the substance and the volume of the dilatometer, it is possible to calculate the density of the substance. Corrections must be made for the coefficient of expansion of the mercury and the dilatometer and for buoyancy of the air.

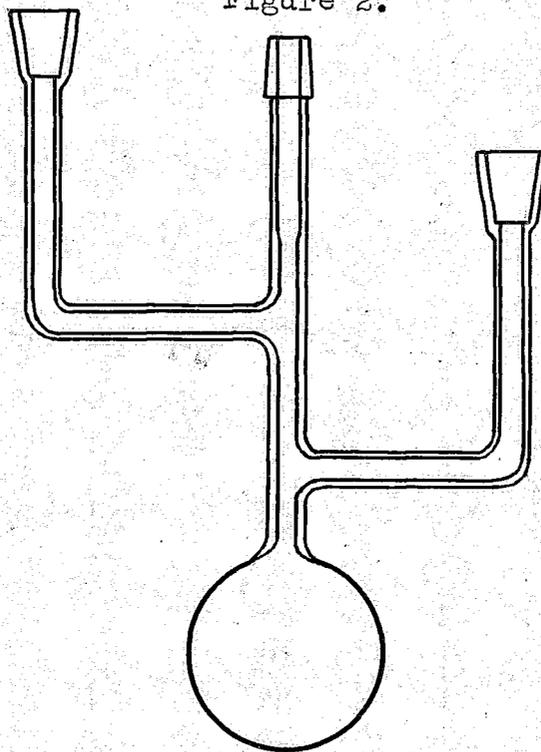
## (2) Preparation of Dilatometer.

The capillary tube for the dilatometer was selected from a piece of small bore capillary tubing of uniform diameter. The diameter of the tube was determined by measuring the length of a weighed amount of mercury at centimeter intervals.

A glass bulb approximately 2 cm. in diameter was then blown from heavy pyrex tubing. Before weighing the bulb was cleaned with dechromate cleaning solution and dried by washing with absolute alcohol and heating to 50°C. The hydrocarbon was then placed in the bulb and the weight determined. The capillary tubing was then sealed on and mercury distilled into the bulb under a pressure of  $1 \times 10^{-4}$  mm. The dilatometer was then weighed and placed in bath.

Some difficulty was encountered in placing the hexamethylethane in the bulb. The high vapour pressure and the narrow liquid range of the compound made it difficult to handle. Two methods were used.

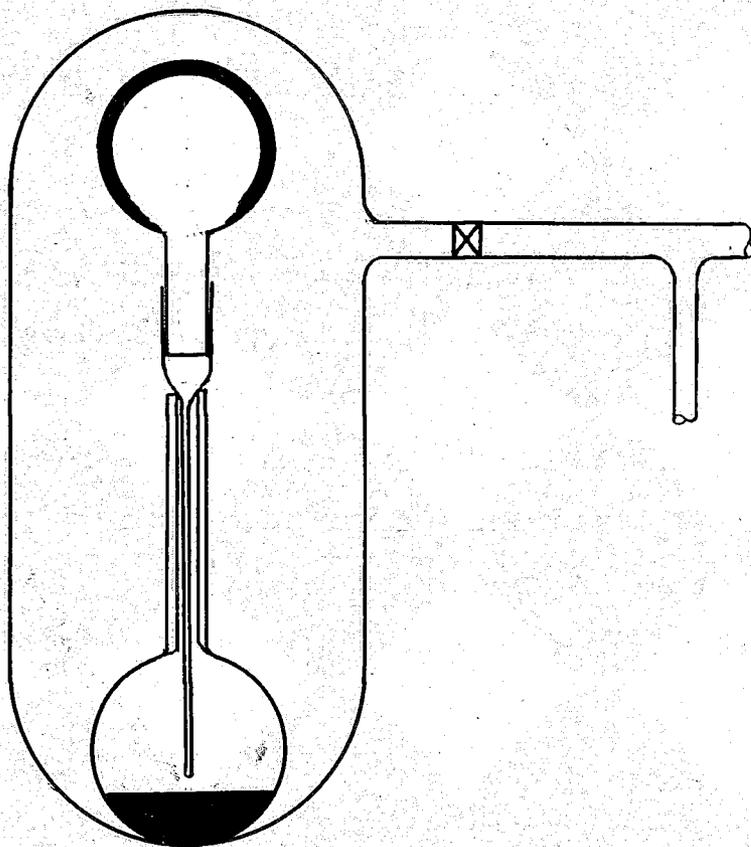
Figure 2.



A diagram of the apparatus first used in filling the bulb is shown in Figure 2. The dilatometer bulb is shown with three ground glass connections, one for the hexamethylethane, one for applying a vacuum, and the last for the distilled mercury. The bulb was evacuated and heat applied to the bulb containing the hexamethylethane. Dry ice was packed around the dilatometer bulb to condense the sublimed hexamethylethane. Although most of the compound condensed in the bulb some also crystallized in the capillary tubing and in the mercury reservoir. It was found possible to remove all of the hydrocarbon from the wall of the capillary tubing by heating but some always recrystallized back on the tubing when cooled.

To prevent the formation of crystals on the capillary walls it was decided to melt the hexamethylethane under pressure and pour it into the bulb. A diagram of the apparatus is shown in Figure 3.

Figure 3.



The dilatometer bulb was sealed in a tube with a small funnel and the bulb of hexamethylethane. The tube was then evacuated and hydrogen gas admitted until the pressure was 25 lbs. per sq. in. As the apparatus was heated the hexamethylethane melted and flowed freely through the funnel into the dilatometer bulb. The bulb was removed from the tube, weighed accurately, and the capillary tube sealed on. The mercury was distilled into the bulb under a pressure of

$1 \times 10^{-4}$  mm.

Calibration of the dilatometer was left until the end of the investigation when the mercury was removed and weighed, and the dilatometer cleaned of all the hydrocarbon. Mercury was distilled in under a pressure of  $1 \times 10^{-5}$  mm. and the level of the mercury noted at different temperatures. In this way it was possible to determine the volume of the dilatometer and check the bore of the capillary. All weights were corrected for buoyancy.

In previous dilatometer work done in this laboratory much smaller samples of hydrocarbon were used (1 gm. in place of 3.9 gms.). It was believed that this would give the dilatometer increased sensitivity. This made it necessary, however, to remove mercury several times during the course of the work. The weight of mercury varied from 86.0971 grams for lower temperatures to 70.0516 grams for the melting region.

### (3) Temperature Control.

A constant temperature bath was used to obtain constant temperatures. The bath was a pyrex glass cylinder 25 cm. in diameter and 46 cm. high and was fitted with a stirrer, variable heating coil controlled by a precision-thermo-regulator, and a stand for the dilatometer. The bath assembly is shown in Figure 4. For temperatures below 70°C water was used in the bath but was replaced by Stanolax oil at higher temperatures because of large temperature losses.

At first temperature control was maintained by

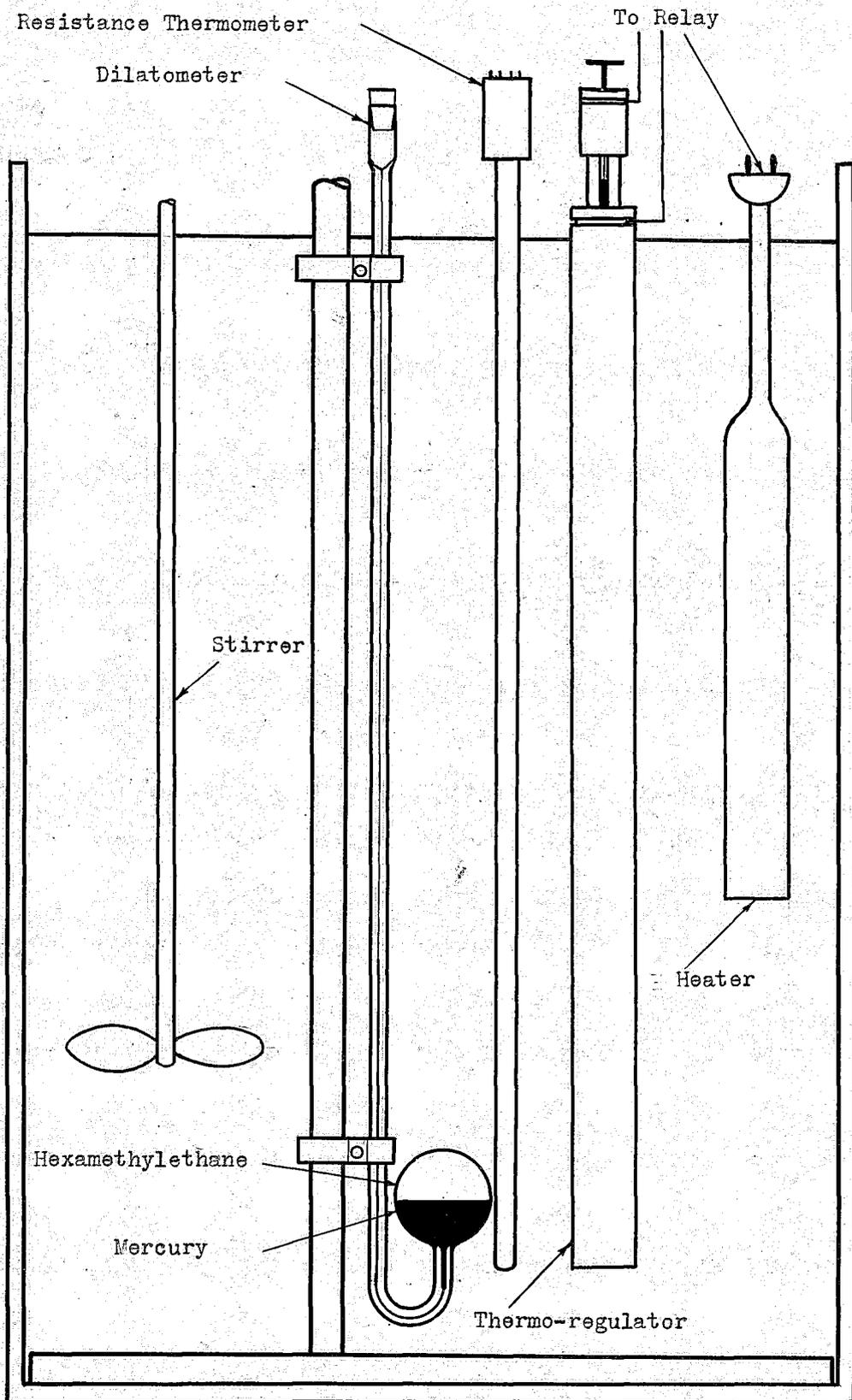


Figure4. Thermostat Assembly.

means of the thermo-regulator but it was found that the temperature varied as much as  $0.1^{\circ}\text{C}$ . In the actual experimental work the degree of heating was adjusted by insulating the bath and immersing a 100 watt lamp in the oil. The temperatures at which density measurements were made are within  $\pm 0.02^{\circ}\text{C}$  of the recorded values.

#### (4) Experimental Observations.

The only experimental measurements required for the density determinations were the temperatures and corresponding capillary heights. All temperature measurements were obtained from a platinum resistance thermometer (#169134). The thermometer had been calibrated by the U. S. Bureau of Standards. The capillary heights were measured with a cathetometer graduated in 0.001 mm. It was not possible, however, to check readings any closer than  $\pm 0.004$  mm. The mercury column was illuminated from behind the bath to facilitate reading the capillary heights.

It was found that the time required for the hydrocarbon to reach its final state at any one temperature varied from 15 minutes to 48 hours depending on the region being examined. Equilibrium was reached in a few minutes with temperatures up to  $80^{\circ}\text{C}$  and in the melting region. In this case readings were taken every half hour. Above  $80^{\circ}\text{C}$  it was found that several hours elapsed before a state of equilibrium was reached. At the transition and setting points it was found that 48 hours was required. In general, equilibrium was reached more rapidly when the temperature

intervals were kept fairly large. Small intervals of  $0.1^{\circ}\text{C}$  sometimes required two or three hours before equilibrium was reached.

## RESULTS.

### (1) Capillary Heights.

From the discussion of the dilatometer method already given it is readily seen that if the capillary is of uniform diameter the general shape of the density-temperature curves can be obtained simply by plotting the capillary heights against the resistance of the platinum resistance thermometer. In the case, the sample of hydrocarbon was so large that mercury had to be removed every  $20^{\circ}$  or so with the result that the curve was not continuous. It was possible, however, to determine any discrepancy in the densities in the region being examined. Wherever possible capillary readings were checked with increasing and decreasing temperatures.

### (2) Calibration of Capillary Tube.

The bore of the capillary tube was determined by measuring the length of a known weight of mercury at centimeter intervals along the length of the tube. These results were later checked at different temperatures when the bulb was filled with mercury. These results checked very closely. The average area determined by the first method was  $0.0039315$  sq. cm. One calculation of the area determined by the second method is given.

Mass of mercury = 149.2362 gms.

Volume at 84.80°C = 11.146631 ccs.

Volume at 43.94°C = 11.063626 ccs.

Difference in volume = 0.083005 ccs.

Correction for expansion of glass

= (40.86)(11.063626)(0.0000096) = 0.004340 ccs.

Net expansion of mercury = 0.078665 ccs.

Difference in mercury levels = 19.853 cms.

Area of cross-section =  $\frac{0.078665}{19.853}$  = 0.003962 sq. cm.

### (3) Calculation of Densities.

The following symbols are used:

t = temperature at which readings were taken - °C.

h = height of mercury above zero reference mark.

A = cross-sectional area of the capillary tube.

$V_{20}^{\circ}$  = Volume of the bulb to the zero point at 20°C.

$V_{20}^h$  = Total volume to height h at 20°C.

=  $V_{20}^{\circ} + hA$ .

$V_t^h$  = Total volume to height h at t°C.

=  $V_{20}^h + V_{20}^h(t-20)a$ , where  $a = 0.0000096$  cc/cc/°C,

the coefficient of expansion of pyrex glass.

W = total mass of mercury in dilatometer with hydrocarbon.

$V_t$  = Volume of mercury in dilatometer at t°C (see appendix).

w = mass of hydrocarbon in bulb.

$v_t$  = volume of hydrocarbon in bulb at t°C.

=  $V_t^h - V_t$

Dt = density of hydrocarbon at t°C.

=  $\frac{w}{v_t}$

## Example of Calculations:

All density calculations were made in the same manner.

$$t = 91.50^{\circ}\text{C}$$

$$h = 30.509 \text{ cms.}$$

$$A = 0.00393 \text{ sq. cm.}$$

$$hA = 0.12026 \text{ ccs.}$$

$$V_{20}^{\circ} = 11.05358 \text{ ccs.}$$

$$V_{20}^h = V_{20}^{\circ} + hA = 11.05358 + 0.12026 = 11.17384 \text{ ccs.}$$

$$V_t^h = 11.17384 + 11.17384 (91.50 - 20.00) (0.0000096) \\ = 11.18151 \text{ ccs.}$$

$$W = 82.6576 \text{ gms.}$$

$$V_t = (82.6576) (0.0747816) = 6.18127 \text{ ccs.}$$

$$v_t = V_t^h - V_t = 11.18151 - 6.18127 = 5.00024 \text{ ccs.}$$

$$w = 3.8851 \text{ gms.}$$

$$D_t = \frac{w}{v_t} = \frac{3.8851}{5.00024} = 0.7770 \text{ gms/cc.}$$

10003  
0006

TABLE 3

<u>Temp.</u>	<u>Density</u>	<u>Temp.</u>	<u>Density</u>
20	0.8242	36.12	0.8151
20.69	0.8240	36.43	0.8149
21.18	0.8237	37.31	0.8144
22.12	0.8231	38.96	0.8132
24.36	0.8221	39.55	0.8131
25.06	0.8217	41.73	0.8117
25.21	0.8214	43.53	0.8107
25.67	0.8210	43.59	0.8106
26.73	0.8207	43.90	0.8103
26.96	0.8206	45.24	0.8097
27.75	0.8199	48.30	0.8075
27.98	0.8198	51.78	0.8055
30.28	0.8193	52.07	0.8051
31.57	0.8178	56.93	0.8021
31.75	0.8174	58.11	0.8010
33.15	0.8168	58.61	0.8008
33.92	0.8164		

<u>Temp.</u>	<u>Density</u>	<u>Temp.</u>	<u>Density</u>
61.86	0.7989	100.00	0.7645
63.66	0.7974	100.10	0.7641
65.12	0.7964	100.14	0.7620
65.76	0.7962	100.25	0.7614
68.01	0.7943	100.28	0.7608
71.53	0.7920	100.35	0.7600
72.62	0.7915	100.40	0.7584
72.89	0.7914	100.44	0.7572
73.05	0.7913	100.50	0.7548
74.51	0.7898	100.56	0.7518
74.82	0.7897	100.60	M.P.
78.75	0.7869	100.59	0.6567
79.87	0.7861	100.71	0.6568
84.52	0.7826	100.84	0.6566
85.55	0.7820	101.18	0.6563
85.97	0.7812	101.92	0.6557
87.72	0.7797	102.26	0.6553
89.23	0.7786	102.58	0.6551
92.07	0.7764	102.64	0.6550
99.48	0.7682	102.80	0.6549
99.92	0.7657	103.42	0.6543
99.98	0.7649		

Descending Temperatures Only.

<u>Temp.</u>	<u>Density</u>	<u>Temp.</u>	<u>Density</u>
99.63	0.7336	93.16	0.7389
99.17	0.7340	90.87	0.7404
98.76	0.7342	89.77	0.7411
98.32	0.7345	89.02	0.7417
98.11	0.7346	87.56	0.7424
97.97	0.7351	86.50	0.7433
97.01	0.7359	85.38	0.7442
96.02	0.7362	84.12	0.7457
95.81	0.7369	83.50	0.7469
94.97	0.7370	82.60	0.7473
94.65	0.7377		

#### (4) Discussion.

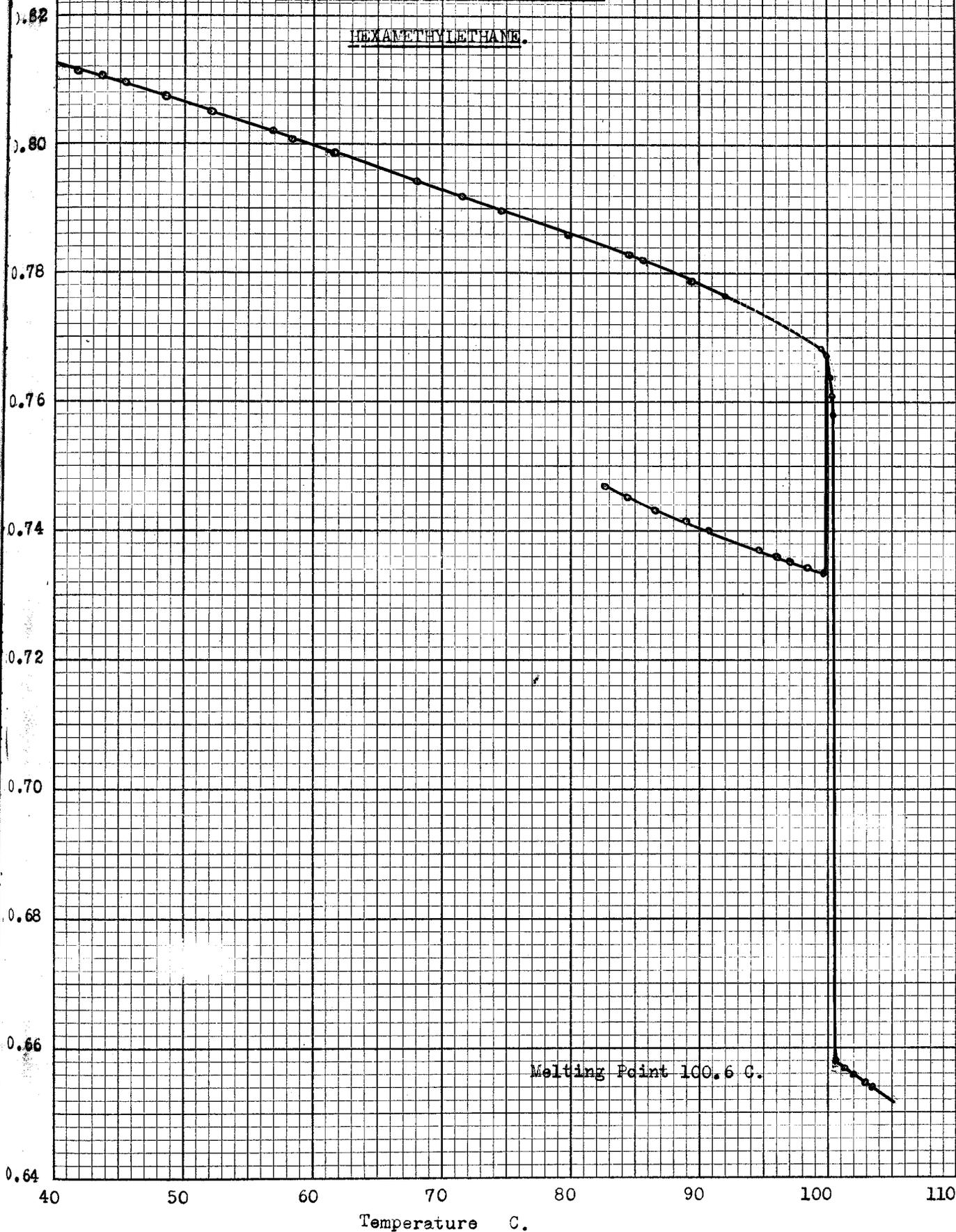
The density-temperature curve for hexamethylethane is given in Figure 5.

In the temperature range between 20° and 92°C the densities were checked with both increasing and decreasing temperatures at least twice. Every 20° or so it was found necessary to remove some mercury from the bulb so that

measurements could be made at higher temperatures. This was done in each case without melting the hydrocarbon. When mercury was removed from the bulb to measure the density between  $92^{\circ}$  and the melting point the hydrocarbon was melted. It can be seen from the density-temperature that the hexamethylethane solidified in a different phase. Hence there is a region where hexamethylethane has two densities at one temperature, representing two crystalline phases. It was not realized during the measurements that two phases existed and as a result there is a blank space in the density curve. It was noted, however, that it was impossible to obtain consistent readings in this region. It was later found that the mercury tended to stick in the capillary tube when the temperature was lowered. Only one set of measurements has been obtained for this phase between  $82^{\circ}\text{C}$  and  $99^{\circ}\text{C}$ . The existence of a similar hysteresis in the density-temperature curve has been determined by Keays for the normal paraffin hydrocarbons C18, C20, and C22.

Some difficulty was encountered in obtaining good readings between  $99.5^{\circ}\text{C}$  and  $100.5^{\circ}\text{C}$ . Until the presence of the dense phase had been detected the hydrocarbon was usually solidified at  $98^{\circ}\text{C}$ . To determine the density of the hexamethylethane just below the melting point the temperature was first set at  $100.4^{\circ}\text{C}$  and then dropped to  $100.1^{\circ}\text{C}$  after 48 hours. In this region the temperature had to be controlled within  $0.1^{\circ}\text{C}$  or less before accurate readings could be made. The dense region could be determined with both increasing and decreasing temperatures

DENSITY-TEMPERATURE CURVE FOR  
HEXAMETHYLETHANE.



Melting Point 100.6 C.

showing that supercooling was not present. On one occasion the dense region was supercooled to  $98.0^{\circ}\text{C}$ . Apparently the dense region between  $99.9^{\circ}\text{C}$  and  $100.6^{\circ}\text{C}$  is not stable.

Density measurements in the liquid range were obtained readily. Readings were reproduced several times. The melting point of the hexamethylethane was found to be  $100.60^{\circ}\text{C}$ .

### Treatment of Results.

1. The density-temperature curve for hexamethylethane has been plotted from the results obtained and is given in Figure 4. The melting point of the sample was found to be  $100.6^{\circ}\text{C}$  and a transition point was found to exist between  $65^{\circ}\text{C}$  and  $80^{\circ}\text{C}$ . The less dense phase is apparently unstable between  $99.9^{\circ}\text{C}$  and  $100.6^{\circ}\text{C}$ . Density determinations have not been made between  $92^{\circ}$  and  $90^{\circ}\text{C}$  for the more dense phase between  $60^{\circ}\text{C}$  and  $82^{\circ}\text{C}$  for the less dense phase. The melting point is definitely lower than that given by Doss ( $101.6^{\circ}\text{C}$ ).<sup>4</sup>

2. From the density-temperature curve the density equation was established for the liquid region

$$Dt = 0.6568 - 0.00089(t - 100.6)$$

where  $Dt$  is the density at any temperature  $t^{\circ}\text{C}$ .

The extrapolated liquid density at  $20^{\circ}\text{C}$  is  $0.7288$  gms/cc. This agrees fairly well with the result  $0.7219$  gms/cc. obtained by G. Calingaert<sup>1</sup> from solutions of hexamethylethane in n-octane. The coefficient  $0.00089$  agrees fairly well with average value  $0.00085$  obtained by Calingaert for several branches hydrocarbons. The density

coefficient is larger than the value 0.00064 given by Yatabe for n-tetracosane.

3. The density for hexamethylethane at 20°C is 0.8230. This compares fairly well with the value 0.83<sup>22</sup> given by West.

4. The coefficient of expansion of the liquid was calculated to be 0.0013513 cc/cc/°C. The specific volume equation for the liquid hexamethylethane is then:

$$V_t = 1.5226 (1 + 0.0013513(t - 100.6))$$

where  $V_t$  is the specific volume at any temperature  $t$ °C.

The molecular volume of the liquid hexamethylethane at 20°C was calculated to be 156.42 ccs. This fits fairly well in the curve given by Calingaert.<sup>2</sup>

#### SUMMARY.

The density of hexamethylethane has been determined between 20°C and 103°C. There is a region between 92°C and 99°C for the dense phase and between 60° and 82°C for the less dense phase where the densities have not been determined. The existence of a hysteresis in the density curve has been established but the transition temperature between the two phases has not been determined. The temperature at which the less dense phase reverts to the more dense phase has been determined (99.9°C).

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APPENDIX

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

The following values for the specific volume for mercury were used:

<u>Temp.</u>	<u>Spec.Vol.</u>	<u>Temp.</u>	<u>Spec.Vol.</u>
20.0	0.0738233	63.0	4246
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	0.0744650
26.0	9036	69.0	4785
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	1223	86.0	7074
44.0	0.0741426	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	0.0748423
54.0	2768	97.0	558
55.0	2903	98.0	693
56.0	3037	99.0	828
57.0	3171	100.0	963
58.0	3305	101.0	0.0749008
59.0	3440	102.0	143
60.0	3573	103.0	278
61.0	3708	104.0	413
62.0	4112	105.0	548