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## SEPARATION OF 1,2,4-TRIMETHYLCYCLOHEXANE AND AN ISONONANE FROM A MIDCONTINENT PETROLEUM<sup>1</sup>

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### ABSTRACT

A fraction of Oklahoma petroleum boiling at 141° C, from which the aromatic hydrocarbons previously had been removed, was separated by distillation at 215 mm Hg into a fraction containing the bulk of a naphthene constituent and one enriched in paraffins. From the former, nearly pure 1,2,4-trimethylcyclohexane was isolated by crystallization from solution in liquid dichlorodifluoromethane. Continued distillation of the paraffinic fraction at normal pressure, alternated with distillation at 215 mm Hg, yielded a fraction containing 85 mole percent of an isononane, probably 2,3-dimethylheptane. The 1,2,4-trimethylcyclohexane constitutes about 0.1 percent, and the isononane about 0.05 percent of the original petroleum.

Effective separation of a paraffin-naphthene mixture, constant-boiling at normal pressure, by distillation at a different pressure arises from the greater change in boiling point with pressure of the naphthene component. For hydrocarbons normally boiling near 140° C, the mean interval between boiling points at 760 mm Hg and 215 mm Hg is about 42° C for paraffins, and about 43.2° C for naphthenes. The boiling points at the two pressures were determined for six hydrocarbons, 2,6-dimethylheptane, a nonanaphthene (boiling at 136.7° C), 1,2,4-trimethylcyclohexane, 4-methyloctane, 3-methyloctane, and 2-methyloctane. The boiling points at these pressures for the "2,3-dimethylheptane" were estimated from values for an impure sample.

The boiling point, freezing point, density, refractive index, and critical solution temperature in aniline have been determined for the 1,2,4-trimethylcyclohexane and the isononane. Comparison of the properties of the 1,2,4-trimethylcyclohexane with those reported for its synthetic stereoisomers indicates that the petroleum hydrocarbon is either 1<sub>cis</sub>, 2<sub>trans</sub>, 4<sub>cis</sub>-trimethylcyclohexane or 1<sub>cis</sub>, 2<sub>trans</sub>, 4<sub>trans</sub>-trimethylcyclohexane.

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## I. INTRODUCTION

In 1883 Markownikoff and Ogloblin [1]<sup>4</sup> identified 1,2,4-trimethylcyclohexane (hexahydropseudocumene) in Caucasian petroleum from the product of its nitration. Since then, frequent allusions have been made to the presence of nonanaphthenes ( $C_9H_{18}$ ) in petroleum without specific reference to 1,2,4-trimethylcyclohexane. Recently, however, Kasansky and Eliséeva [2] dehydrogenated the nonanaphthene fraction, distilling between 135° and 138° C, of Baku petroleum into aromatic material, and, by brominating the portion of the product which boiled at 170° C, obtained some tribromopseudocumene. From this experiment, they concluded that 1,2,4-trimethylcyclohexane was a constituent of the original petroleum fraction.

The present investigation has resulted in the isolation of 1,2,4-trimethylcyclohexane and the partial separation of a nonane, probably 2,3-dimethylheptane, from the methyloctane fraction [3] of an Oklahoma petroleum. Until now, the presence in petroleum of the isononane (boiling point, 140.7° C) appears to have escaped detection.

## II. PREVIOUS FRACTIONATION OF THE PETROLEUM DISTILLATE

After a systematic distillation of the whole naphtha fraction of the petroleum, the material boiling between 130° and 145° C was treated with liquid sulfur dioxide to extract the bulk of the aromatic hydrocarbons [4]. To complete the removal of aromatic material, the immiscible portion was redistilled, and the large-volume fraction boiling between 140° and 145° C was treated with silica gel [3]. The residual oil consisting of paraffins and naphthenes was then distilled at a pressure of 215 mm Hg through a fractionating column, packed with jeweler's locket chain, having the equivalent of about 60 theoretical plates [5]. The distilled material was recovered in 50-ml fractions. After the measurement of their boiling points and refractive indices, fractions boiling within a range of 0.2° C were combined. The distillation separated the material into two main portions, each with a boiling range (at 215 mm Hg) of about 1° C. The larger, boiling between 101° C and 102.2° C (143° and 144.2° C at 760 mm Hg), contained the three methyloctanes. The isolation of these hydrocarbons from the petroleum has already been described [3]. The other portion distilled chiefly between 98° and 99° C. The volumes and refractive indices of the combined fractions comprising this portion are given in figure 1.

<sup>4</sup> Figures in brackets indicate the literature references at the end of this paper.

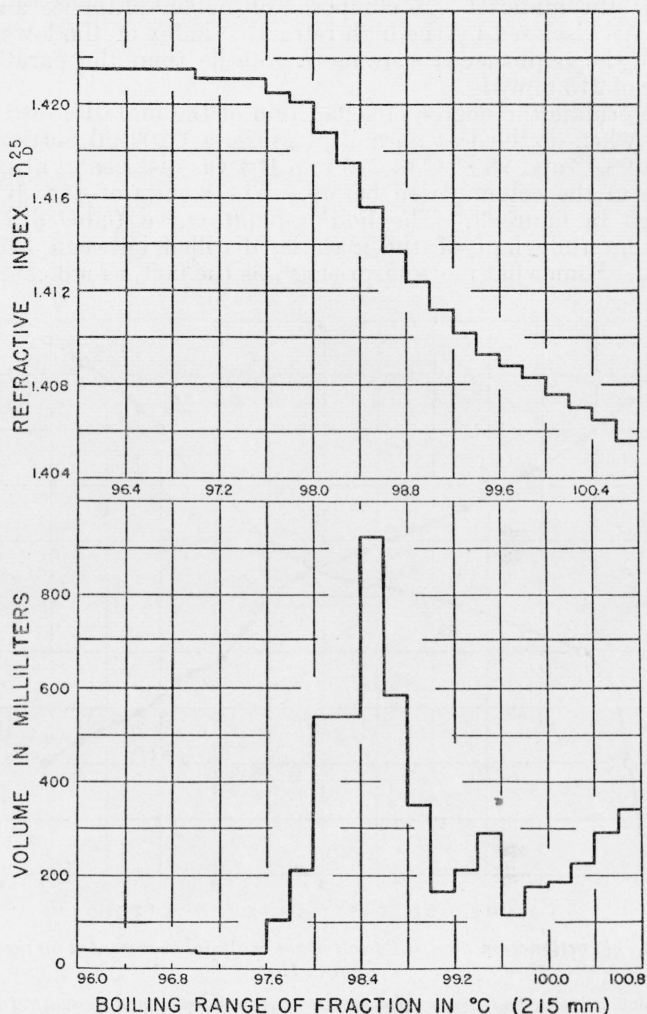


FIGURE 1.—Volumes and refractive indices of the petroleum fractions, boiling between 96.0° and 100.8° C at 215 mm Hg, after removal of aromatic hydrocarbons and subsequent distillation.

Lower graph, volume distribution with respect to boiling range; upper graph, refractive indices.

### III. COMPOSITION AND PROPERTIES OF THE FRACTION BOILING BETWEEN 98° AND 99° C AT 215 mm Hg

In figure 2 the boiling points and refractive indices of the material represented in figure 1 are plotted against the volume distilled. The refractive indices are those for the 50-ml fractions which marked a rise of 0.2° C in the boiling point of the distillate. The plateau in the boiling-point curve between 98° and 99° C represents nearly 3 liters of material whose gradual change in properties indicated it to be a mixture. The values of the boiling points and refractive indices signi-

fied that the material was composed of nonanaphthenes and isononanes. As disclosed by the high refractive index of the lower-boiling material, the naphthenes were more volatile than the paraffins at a pressure of 215 mm Hg.

To determine the degree of separation of the material into its components when distilled at normal pressure, a 1,200-ml portion boiling between 98.4° and 98.8° C at 215 mm Hg was distilled at atmospheric pressure in the column used before. The results of the distillation are given in figure 3. The boiling-point curve (labeled 760 mm) shows that fully half of the material distilled between 141.0° and 141.1° C. Somewhat more surprising was the fact, as indicated by the

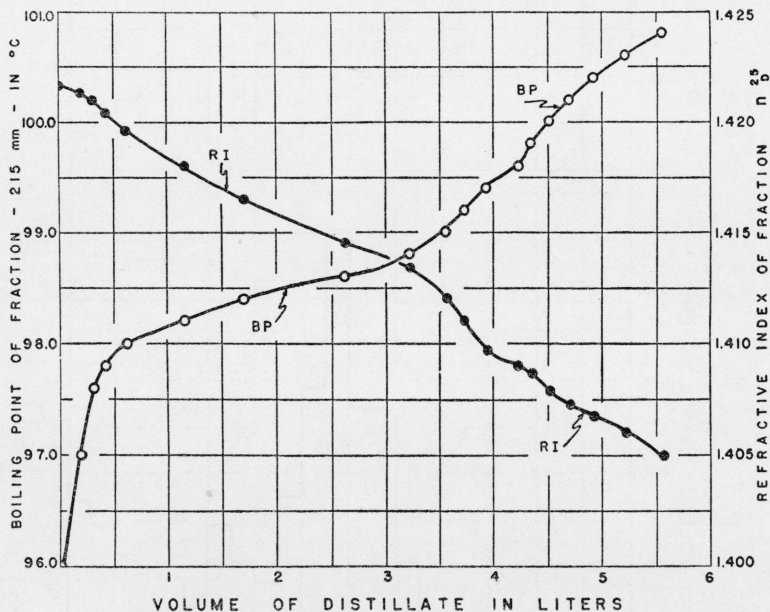


FIGURE 2.—Fractionation by distillation of the material represented by the graphs in figure 1.

Boiling points and refractive indices are plotted against the volume of material distilled. The individual points are those for 50-ml fractions which marked a rise of 0.2° C in the boiling point of the material.

refractive-index curve drawn through the open circles, that at 760 mm Hg the order of distillation of the constituents was the reverse of that at 215 mm Hg. At normal pressure the paraffinic material was more volatile than the naphthene and tended to concentrate in the lower-boiling fractions.<sup>5</sup> It was hoped that the normal boiling points of the component hydrocarbons could be located by the atmospheric distillation and compared with those of known hydrocarbons to obtain a clue as to what compounds might be present. Little knowledge was obtained concerning the boiling points of the constituents. What fractionation there was indicated that the naphthene present boiled above 141.0° C and the paraffin below.

<sup>5</sup> Prior to this experiment, S. T. Schicktanz had observed similar behavior of material from the "isodecane" fraction of this petroleum.



Since it was difficult to fractionate the material at normal pressure, the fractions were combined and distilled again at 215 mm Hg. The change in composition of the material as the distillation progressed is indicated by the curves passing through the solid circles in figure 3. The continual rise in boiling point and the marked change in refractive index indicated that better separation took place at the reduced pressure.

By combustion analysis the composition of a fraction of the distillate boiling at  $98.4_5^\circ\text{C}$  ( $n_D^{25}=1.4151$ ) was 48 mole percent of naphthenes and 52 mole percent of isononanes. The cooling curve of a

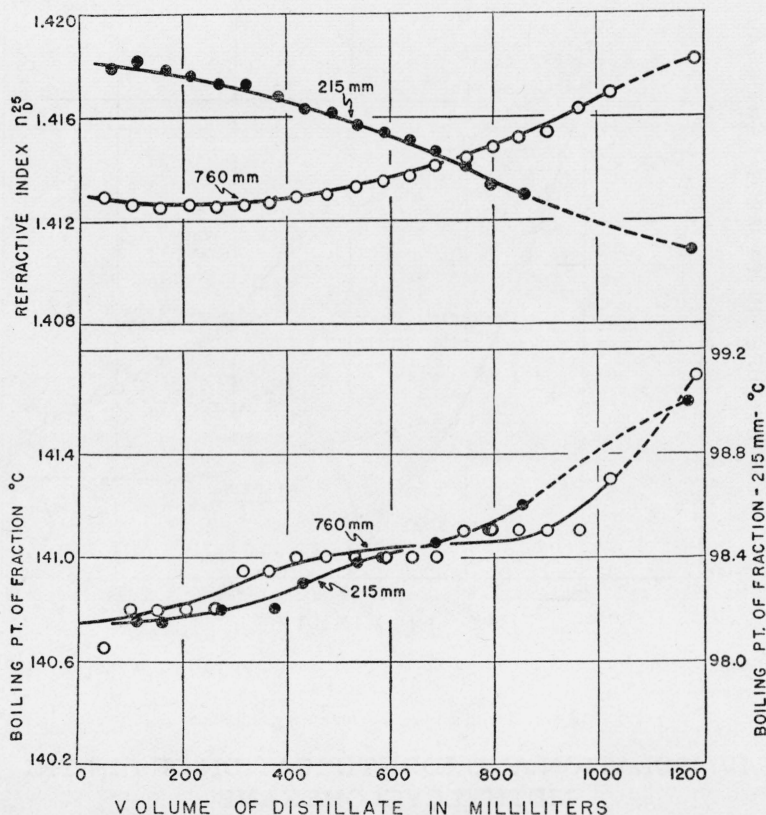


FIGURE 3.—Fractionation of the paraffin-naphthene mixture by distillation at normal pressure contrasted to that obtained by distillation at 215 mm Hg.

Curves passing through the open circles represent the change in boiling point and refractive index of the fractions obtained from the distillation at 760 mm Hg. Curves passing through the solid circles denote the fractionation at 215 mm Hg.

50-ml fraction boiling at  $98.4_5^\circ\text{C}$ , ( $n_D^{25}=1.4154$ ) is shown in figure 4. By repeatedly plunging a metal rod, chilled with liquid air, into the material as it was cooled, freezing was finally induced at  $-120^\circ\text{C}$ . On warming the partially frozen mass, a rapid change from a higher to a lower viscosity took place around  $-115^\circ\text{C}$ , and at  $-104^\circ\text{C}$  the last of the crystals melted. The cooling and warming behavior indicated that the material was substantially a binary mixture. As de-

terminated later, the portion of the melting curve, figure 4, extending from  $-115^{\circ}\text{C}$  to  $-104^{\circ}\text{C}$  represents the melting of the naphthene component, while the break in the curve at  $-115^{\circ}\text{C}$  is attributed to a change in state of the isomeric nonane present (see section VII).

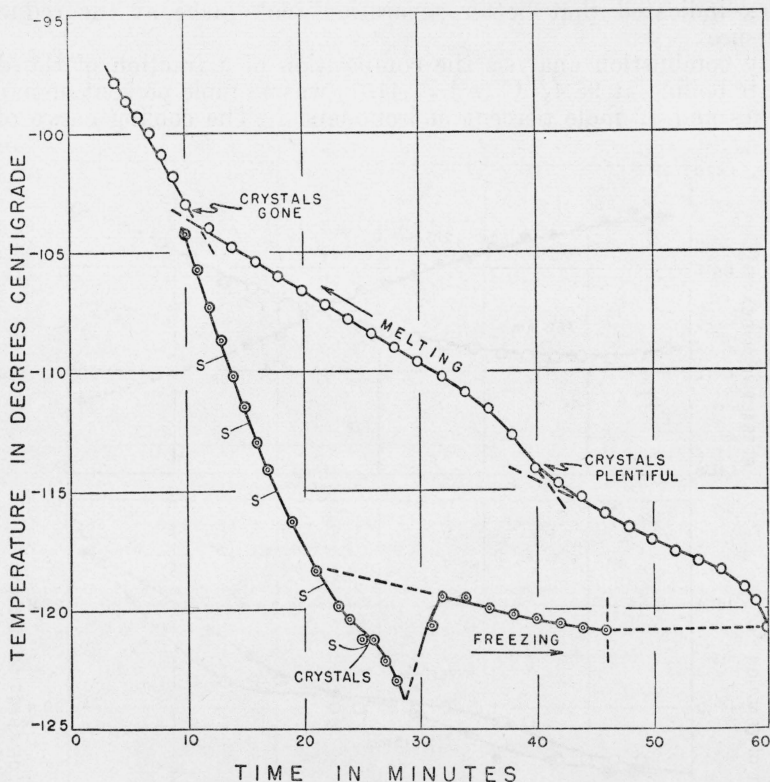


FIGURE 4.—Cooling and warming curves of a distillation fraction boiling at  $98.4^{\circ}\text{C}$  at 215 mm Hg.

S, stirred with a cold rod to induce crystallization.

#### IV. ISOLATION AND IDENTIFICATION OF 1,2,4-TRIMETHYLCYCLOHEXANE

When the material boiling at  $98.4^{\circ}\text{C}$  was mixed with liquid dichlorodifluoromethane, Freon 12, and cooled, a crystal fraction was produced which was found to be enriched in a naphthene having a normal boiling point of approximately  $141.3^{\circ}\text{C}$ . Systematic crystallization from this solvent, alternated with distillation, yielded from the material boiling between  $97.0^{\circ}$  and  $98.8^{\circ}\text{C}$  at 215 mm Hg somewhat more than a liter of the impure naphthene.<sup>6</sup> This was subjected to further fractional crystallization to yield a 95-ml fraction of "best"

<sup>6</sup> The lowest-boiling mother liquor contained another naphthene, probably 1,3,5-trimethylcyclohexane. The higher-boiling mother liquors were rich in paraffins.

naphthene. After distillation through a small fractionating column and filtration through silica gel to remove remaining traces of solvent, this fraction had the following properties: <sup>7</sup>

Normal boiling point, °C	141.22
Pressure coefficient, °C/mm Hg at 760 mm	0.051
Melting point, °C	-86.4
Density at 20° C, g/ml	0.7720
Refractive index, $n_D^{20}$	1.4266
Critical solution temperature in aniline, °C	59.0

The freezing range of 1° C in the cooling curve, figure 5, showed that the compound was sufficiently pure for use in identification. Combustion analysis indicated that its chief impurity was an isomeric nonane. As a result of three determinations by the procedure described by Rossini [6], the mean ratio, moles H<sub>2</sub>O/moles CO<sub>2</sub>, was found to be 1.0060 ± 0.0004. Compared with the theoretical value of 1.0000 for a naphthene, C<sub>n</sub>H<sub>2n</sub>, and 1.1111 for a nonane, C<sub>9</sub>H<sub>20</sub>, the combustion analysis indicated that the material was composed of 94.6 mole percent of a naphthene and 5.4 mole percent of an isononane.

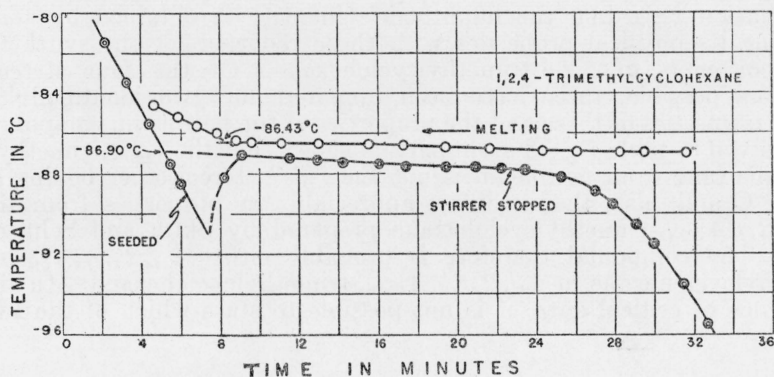


FIGURE 5.—Time-temperature cooling and warming curves of the 1,2,4-trimethylcyclohexane isolated from petroleum.

The molecular weight of the fraction, determined by the lowering in freezing point of cyclohexane,<sup>8</sup> was 128.5, which agrees within the error of the method with the theoretical value of 126.2 for a nonanaphthene, C<sub>9</sub>H<sub>18</sub>.

The nonanaphthene was identified as 1,2,4-trimethylcyclohexane by dehydrogenation over palladinized asbestos (20 percent of palladium). The catalyst was prepared by the method described by Zelinsky and Borisoff [7]. A 5-ml portion of the petroleum hydrocarbon, having  $n_D^{25}=1.4229$ , was vaporized at the rate of six drops a minute and passed through a tube containing a 50-cm section of the catalyst held at a temperature of 340° to 380° C. The passage required 25 minutes, during which time hydrogen was constantly evolved. A hydrocarbon product of 3.2 ml was obtained which had a refractive index at 25° C of 1.4827, and smelled strongly of pseudocumene (1,2,4-trimethylbenzene). This aromatic material was sulfon-

<sup>7</sup> The boiling point was measured in a Świątosławski ebulliometer. The difference between the boiling and condensing points was found to be 0.013° C. The density was determined by the Division of Weights and Measures of this Bureau.

<sup>8</sup> A value of 7.4 cal/g was used for the heat of fusion of cyclohexane. See Parks and Huffman, *Ind. Eng. Chem.* **23**, 1138 (1931).

ated at 45° C with a mixture of 20 ml of concentrated sulfuric acid and 1 ml of fuming sulfuric acid (30 percent of free SO<sub>3</sub>) and then hydrolyzed by steam distillation. After rejecting the oil distilling near 100° C as unsulfonated material, 1.3 ml of hydrocarbon was produced by hydrolysis of the sulfonated material at 145° C. The product had a refractive index at 25° C of 1.5022, as compared with an observed index of 1.5017 for a reference sample of pseudocumene [14]. Confirmatory evidence of the identity of the dehydrogenated naphthene with pseudocumene was obtained by comparing the melting point of the former's nitro derivative with that of pure trinitropseudocumene, and by determining the melting point of a mixture of the two nitro compounds. Comparative values for the three melting points were as follows:

- (1) From the dehydrogenated naphthene..... 180° C.  
 (2) From pseudocumene..... 180° C.  
 (3) For a mixture of (1) and (2)..... 180° C.

The results of the dehydrogenation and nitration experiments leave little doubt that the petroleum naphthene is hexahydropseudocumene, namely, 1,2,4-trimethylcyclohexane. However, further information regarding the naphthene's identity is obtained by comparing its physical properties with those reported for the synthetic stereoisomers of 1,2,4-trimethylcyclohexane. Of the four stereoisomers possible, three have been prepared and two identified [8]. The properties of these and the properties of the petroleum compound are given in table 1. The comparison shows that the 1,2,4-trimethylcyclohexane from petroleum is not the "cis" stereoisomer boiling at 146° C and, also, that it differs appreciably in properties from the 1<sub>cis</sub>,2<sub>cis</sub>,4<sub>trans</sub>-trimethylcyclohexane prepared by Skita and Schneck [8]. The compound therefore is probably either 1<sub>cis</sub>,2<sub>trans</sub>,4<sub>cis</sub>-trimethylcyclohexane or 1<sub>cis</sub>,2<sub>trans</sub>,4<sub>trans</sub>-trimethylcyclohexane. In the absence of critical data, it is not possible to state which of the two it is.

TABLE 1.—Comparison of the properties of 1,2,4-trimethylcyclohexane from petroleum with those reported for three of the four stereoisomers of 1,2,4-trimethylcyclohexane<sup>a</sup>

Compound	Boiling point (760 mm Hg)	Density at 20° C	Refractive index
1,2,4-Trimethylcyclohexane from Oklahoma petroleum; White and Glasgow	° C	g/ml	$n_D^{20}$
.....	141.2	0.7720	1.4266
1 <sub>cis</sub> ,2 <sub>trans</sub> ,4 <sub>trans</sub> -Trimethylcyclohexane; Von Auwers [9].....	140 to 141	.777	1.4292
1 <sub>cis</sub> ,2 <sub>cis</sub> ,4 <sub>trans</sub> -Trimethylcyclohexane; Skita and Schneck [8].....	142	.786	1.4321
1 <sub>cis</sub> ,2 <sub>cis</sub> ,4 <sub>cis</sub> -Trimethylcyclohexane; Skita and Schneck [8].....	146	.790	1.4331

<sup>a</sup> The data for the properties of the synthetic compounds have been taken at their face value. Since the values were determined on small samples (5 to 10 g) whose purity was not specified, they are not necessarily accurate values.

<sup>b</sup> If the compound prepared by Von Auwers is 1<sub>cis</sub>,2<sub>trans</sub>,4<sub>trans</sub>-trimethylcyclohexane, the fourth, and unknown, stereoisomer is 1<sub>cis</sub>,2<sub>trans</sub>,4<sub>cis</sub>-trimethylcyclohexane.



### V. COMPOSITION AND PROPERTIES OF THE MATERIAL DISTILLING BETWEEN 98.8° AND 100.8° C AT 215 mm Hg, AFTER PARTIAL REMOVAL OF 1,2,4-TRIMETHYLCYCLOHEXANE

Figure 6 shows the boiling-point and refractive-index curves of 2.3 liters of material obtained by redistilling a mixture of 0.6 liter of the higher-boiling mother liquors from the crystallization of 1,2,4-trimethylcyclohexane and the 2 liters of petroleum distillate boiling between 98.8° and 100.8° C.<sup>9</sup> The comparatively low refractive index indi-

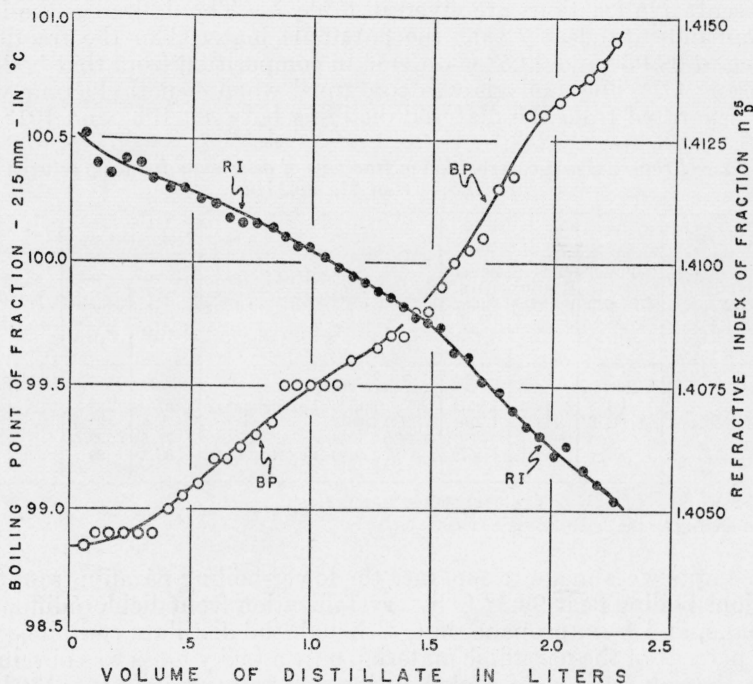


FIGURE 6.—Fractionation by distillation of crystallization residues and petroleum fractions boiling directly above 1,2,4-trimethylcyclohexane.

The circles on the two curves represent, respectively, the boiling points and refractive indices of successive fractions of distillate.

cated that the redistilled material, while still containing some 1,2,4-trimethylcyclohexane, was largely composed of paraffinic hydrocarbons. The shape of the boiling-point curve suggested the presence of at least two paraffins. The indications were that the bulk of the paraffin previously encountered as a binary mixture with the isolated trimethylcyclohexane had been concentrated in the distillate boiling between 98.8° and 99.8° C, and that another paraffin had accumulated in the fractions boiling near 100.7° C. The presence of two paraffins could not be clearly established, however, until the amount of naphthene present had been determined with accuracy. Naph-

<sup>9</sup> Material boiling above 100.8° C had been set aside for the separation of its chief constituent, 2-methyloctane.

thenes differ distinctly from paraffins in the magnitude of their refractive indices, but the amount of naphthene in the apparently three-component system under consideration could not be determined by measuring the refractive index alone, because of a possible difference in refractive index of the paraffinic material in the successive fractions of the distillate. Since, however, the two paraffins had the same molecular weight,<sup>10</sup> the content of the naphthene in the fractions could be determined by combustion analysis, and from the known refractive index of the distillate and the assumption that the naphthene was 1,2,4-trimethylcyclohexane, a refractive index of the residual paraffinic material could be computed. Combustion analyses of representative fractions are given in table 2. The figures in the last column indicate clearly that the paraffinic material in the fractions boiling at 99.05° and 99.5° C differed in composition from that boiling at 100.4° C. The analysis was confirmed when 4-methyloctane was later separated from the material distilling between 100° and 101° C.

TABLE 2.—*Properties and composition of fractions of petroleum distilling between 99° and 100.5° C at 215 mm Hg*

Boiling point of fraction (215 mm Hg)	Boiling point of fraction (760 mm Hg)	$\Delta t$ (boiling point) <sup>a</sup>	Refractive index	Moles H <sub>2</sub> O Moles CO <sub>2</sub>	Estimated mole percentage		Estimated refractive index of paraffin constituent <sup>b</sup>
					Paraffin C <sub>9</sub> H <sub>20</sub>	Naphthene C <sub>9</sub> H <sub>18</sub>	
°C	°C	°C	$n_D^{25}$				$n_D^{25}$
99.0 <sub>5</sub> -----	141.3	42.3	1.4115	1.0740 (1 experiment)	67	33	1.4047
99.5 <sub>6</sub> -----	141.6	42.1	1.4101	(1) 1.0862	77.5	22.5	1.4059
				(2) 1.0861	77.5	22.5	1.4059
100.3 <sub>5</sub> -----	142.4	42.1	1.4070	1.0890 (1 experiment)	80	20	1.4026

<sup>a</sup> Difference between the boiling point at 760 and 215 mm Hg.

<sup>b</sup> Assuming  $n_D^{25}$  for the naphthene to be 1.4250.

Attempts were made to separate the lower-boiling paraffin from the fractions boiling near 99.5° C by crystallization from dichlorodifluoromethane, and from propane, but, although the distillate contained 75 mole percent of the paraffinic material, only a tacky mass was obtained when the solutions were cooled to low temperatures. At -170° C the glue-like material appeared to be insoluble in the solvents used. An effort to fractionate the material which boiled at 98.8° C by distilling it with excess glacial acetic acid [10, 11] was also unsuccessful. Apparently the composition of the fraction was not as simple as was supposed or else the azeotropic properties of the component hydrocarbons were too much alike. A system of fractionation by distillation at normal pressure, alternated with distillation at a pressure of 215 mm Hg, was then tried and found to be fairly successful in separating the chief paraffinic constituent from the fraction boiling between 98.8° and 99.8° C.

<sup>10</sup> It is almost axiomatic that paraffins from petroleum which boil near 140° C are nonanes.

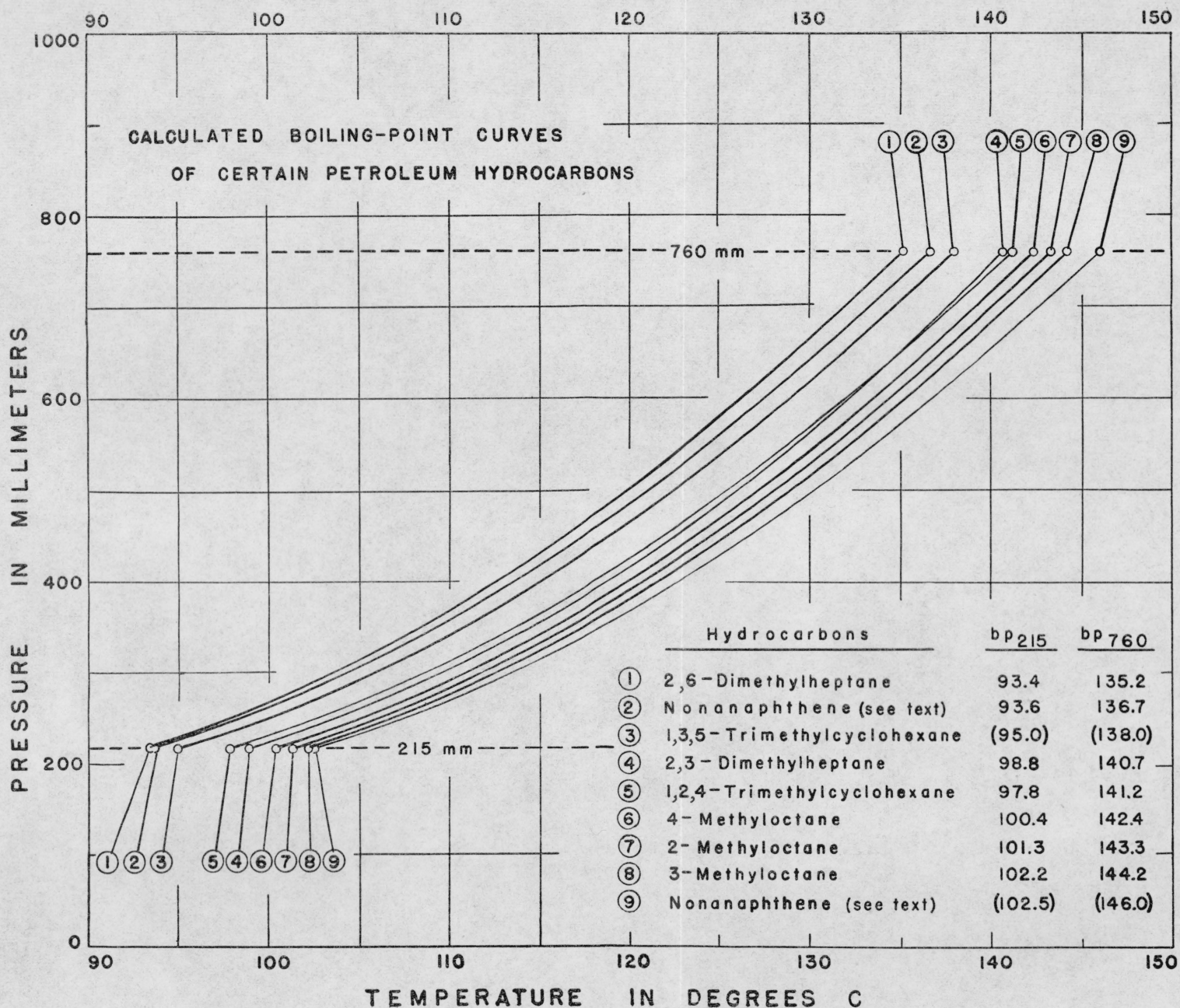


FIGURE 7.—Calculated vapor pressure curves of certain hydrocarbons found in Oklahoma petroleum.

The numbers in circles refer to the curves of the numbered hydrocarbons in the table at the lower right of the figure. The table gives the boiling points, at 760 mm and at 215 mm Hg, of the listed hydrocarbons. Those without parentheses are experimentally determined values, those in parentheses are values estimated from the boiling points of impure fractions. For the mode of construction of the curves, see text.

VI. SEPARATION OF PARAFFIN-NAPHTHENE MIXTURES  
BY ALTERNATE DISTILLATION AT NORMAL AND REDUCED PRESSURES

As pointed out in section III, 1, 2, 4-trimethylcyclohexane has a higher volatility at a pressure of 215 mm Hg than the paraffin associated with it in the petroleum, and a correspondingly lower volatility at 760 mm Hg. This behavior illustrates the general principle that, with paraffins, naphthenes, and aromatic hydrocarbons which boil at nearly the same temperature, members of one class differ materially from those of another class in the change of their vapor pressures with temperature. Because of this, a binary mixture consisting of a paraffin and a naphthene boiling close together can have the partial pressures of its components so altered as to enhance their separation by fractional distillation, or to reverse the order in which they distil [18].<sup>11</sup> Figure 7 shows calculated vapor-pressure curves of the paraffin and naphthene hydrocarbons in the fraction of this petroleum which normally boils between 135° and 145° C. In the lower right of the figure the boiling points at 215 mm and 760 mm Hg are given for the hydrocarbons.<sup>12</sup> The values for boiling points were experimentally determined, except those in parentheses. These were estimated from the boiling points of impure fractions by correcting for the effect of the major impurity. To construct the vapor-pressure curves of figure 7, the reciprocals of the absolute boiling points of 1,2,4-trimethylcyclohexane and of 2-methyloctane were first plotted with respect to the logarithm of the corresponding pressures for the two experimental points (at 215 and 760 mm Hg). Intermediate values for boiling points and pressures were then obtained from the straight line connecting the experimental points. With these additional values, the vapor-pressure curves of the two hydrocarbons were drawn. Lines for the other paraffins were drawn with the same curvature as that for 2-methyloctane, and those for the naphthenes with the same curvature as that for 1,2,4-trimethylcyclohexane. This was permissible because the difference between the boiling points at 760 and 215 mm Hg for each of the paraffins was quite close to the mean value of 42° C, and for each of the naphthenes, close to the mean value of 43.2° C. It should be noted that the curves as constructed may not correspond exactly with the actual vapor pressure curves of the individual hydrocarbons, but they nevertheless illustrate the relative change in vapor pressure with temperature of the two classes of hydrocarbons. All of the curves have been useful in the analysis of the distillate boiling between 135° and 145° C. Curves 1 and 2, for example, indicate the substantial difference between the boiling points at normal pressure of 2,6-dimethylheptane and a nonanaphthene, and the close proximity of

<sup>11</sup> A practical demonstration of the possibilities of the principle is afforded by the experiments of S. T. Schickantz mentioned in footnote 4. The results of the experiments were kindly called to the attention of the authors by Schickantz, prior to the present investigation.

<sup>12</sup> The hydrocarbons used for the boiling-point determinations were, with the exception of 4-methyloctane, the best fractions prepared from petroleum. The sample of 4-methyloctane was supplied by George Calingaert of the Ethyl Gasoline Corporation. Properties of the samples used are listed in the following papers relating to 2,6-dimethylheptane, J. Research NBS 17, 952 (1936) RP955; nonanaphthene, 136.7° C, J. Research NBS 13, 808 (1934) RP745; isononane (probably 2, 3-dimethylheptane), 140.7° C, described in this paper; 1,2,4-trimethylcyclohexane, described in this paper; and 4-methyloctane (Calingaert), 2-methyloctane, and 3-methyloctane, J. Research NBS 19, 423 (1937) RP1033. The fractions containing the nonanaphthene (probably 1,3,5-trimethylcyclohexane) boiling at 138° C, and the nonanaphthene boiling at 146° C, had refractive indices at 25° C of 1.4233 and 1.4263, respectively. The isolation of these compounds from the petroleum has not been completed.



their boiling points at 215 mm Hg. It would be expected that a mixture of these two hydrocarbons could be separated by fractional distillation at 760 mm Hg, but not at 215 mm, at which pressure a constant-boiling mixture would result. This was found to be the case when a fraction of the petroleum composed of these two hydrocarbons was resolved into its constituents [12]. Similarly, use was made of the pressure-temperature relationships depicted in curves 8 and 9, in separating 3-methyloctane from the petroleum [3]. Special attention, however, is called to curves 4 and 5, which concern the present work. Curve 4 crosses curve 5 at a pressure of about 650 mm. In this region of pressure the pair of hydrocarbons form a mixture which is constant-boiling at about 135° C. At higher or lower pressures, the mixture would distil over a definite temperature range. It follows that constant-boiling mixtures of naphthene and paraffin hydrocarbons are only incidental, and that such mixtures may be resolved into their components by distillation at a pressure somewhat removed from that causing the constant-boiling behavior. Closer inspection of curves 4 and 5 indicates that a binary mixture of 1,2,4-trimethylcyclohexane and the "2,3-dimethylheptane" could be separated more readily by distillation at 215 mm Hg than at 760 mm. The present problem, however, was to separate a three-component mixture which contained, besides these two compounds, 4-methyloctane (curve 6). It was believed that by fractionally distilling the mixture at atmospheric pressure, the 4-methyloctane could be removed by rejecting the end fractions and residue which, from the order of distillation of the constituents, would contain the 4-methyloctane and some of the naphthene. The bulk of the lower-boiling paraffin would be concentrated in the initial fractions as a binary mixture with the naphthene which afterwards could be removed by fractionation at a pressure of 215 mm Hg.

#### VII. SEPARATION OF THE PARAFFIN-NAPHTHENE MIXTURE BOILING BETWEEN 98.8° AND 99.8° C AT 215 mm Hg

Using the procedure outlined above, the 1600-ml fraction shown in figure 6 to boil between 98.9° and 100° C was mixed with 400 ml of paraffinic mother liquors obtained from further crystallization of the 1,2,4-trimethylcyclohexane stock, and redistilled at 760 mm. The boiling-point and refractive-index curves of the distillate are shown in figure 8. The individual points denote the boiling points and refractive indices of successive 50-ml fractions. The curves show that the first liter of distillate was almost constant-boiling at 141.0° to 141.1° C, and changed but little in refractive index, 1.409 to 1.410. Both properties indicate a constancy in composition of the material. The 50-ml fraction taken after 900 ml had distilled (bp 141.1° C,  $n_D^{25}=1.4101$ ) contained 20 mole percent of a naphthene and 80 mole percent of a nonane. From the composition, the nonane was calculated to have an index of 1.4065 at 25° C. From this point in the distillation, the remaining material distilled at increasingly higher temperatures and exhibited a steady increase in refractive index. For the 50-ml fraction which marked the 1,750-ml point in the distillation (bp 141.9° C,  $n_D^{25}=1.4130$ ), the naphthene content was 40 mole percent. The calculated refractive index of the paraffinic material in this fraction

was 1.4046 at 25° C as compared with 1.4036 for pure 4-methyloctane. From the analysis it was evident that the naphthene and 4-methyloctane had collected in the end fractions of the distillation, and for this reason the last 400 ml of distillate and the residue were rejected. The first 1,400 ml to distil, which was rich in the lower-boiling paraffin, was redistilled at 215 mm Hg.

As a result of this second distillation at reduced pressure, much of the naphthene still present collected in the first portion to distil, and most of the 4-methyloctane which remained was held in the residue. The 850 ml of oil representing the middle portion of the distillate consisted chiefly of the desired isononane. The individual fractions comprising the middle portion ranged in boiling point from 98.7°

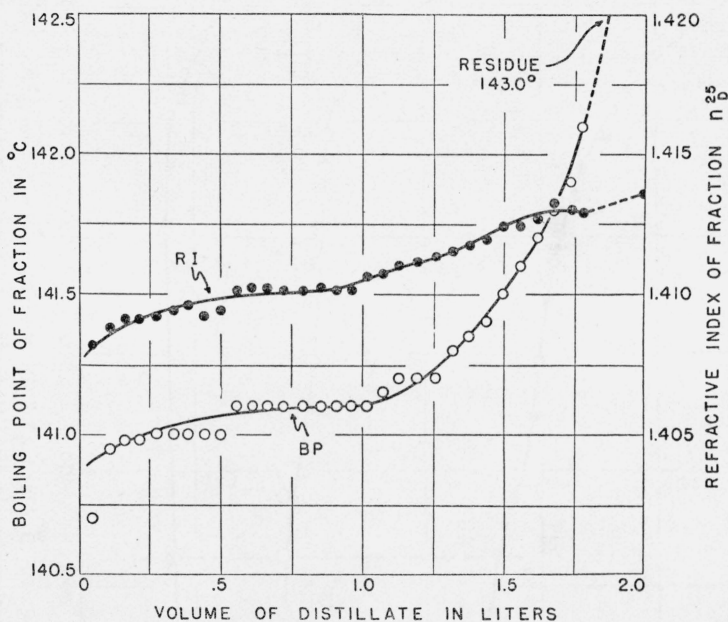


FIGURE 8.—Fractionation by distillation at normal pressure of the petroleum fraction enriched in 2,3-dimethylheptane.

The points on the curves indicate the boiling points and refractive indices of successive fractions.

to 98.9° C and varied in refractive index (in the order distilled) from 1.4125 to 1.4087. By combustion analysis, the naphthene content was 30 mole percent for a fraction with  $n_D^{25}=1.4122$  and 15 mole percent for one with  $n_D^{25}=1.4087$ . The paraffinic material in most of the distillate had a calculated refractive index of 1.406 at 25° C. In the last fractions, however, the index of the paraffinic material had decreased to 1.405.

As a final step in the separation of the isononane, the middle portion (850 ml) of the distillate described above was redistilled in the same column, at 760 mm Hg. The boiling points of the successive fractions from this final distillation were measured at 760 mm and at 215 mm Hg in order to determine the nature of the distillate.

The boiling-point curves for the two sets of data are shown in the lower part of figure 9. The curve at the top of the figure indicates the range in refractive index of the distillate. Barring the first 100 ml of oil distilled, the gradual rise in refractive index of the

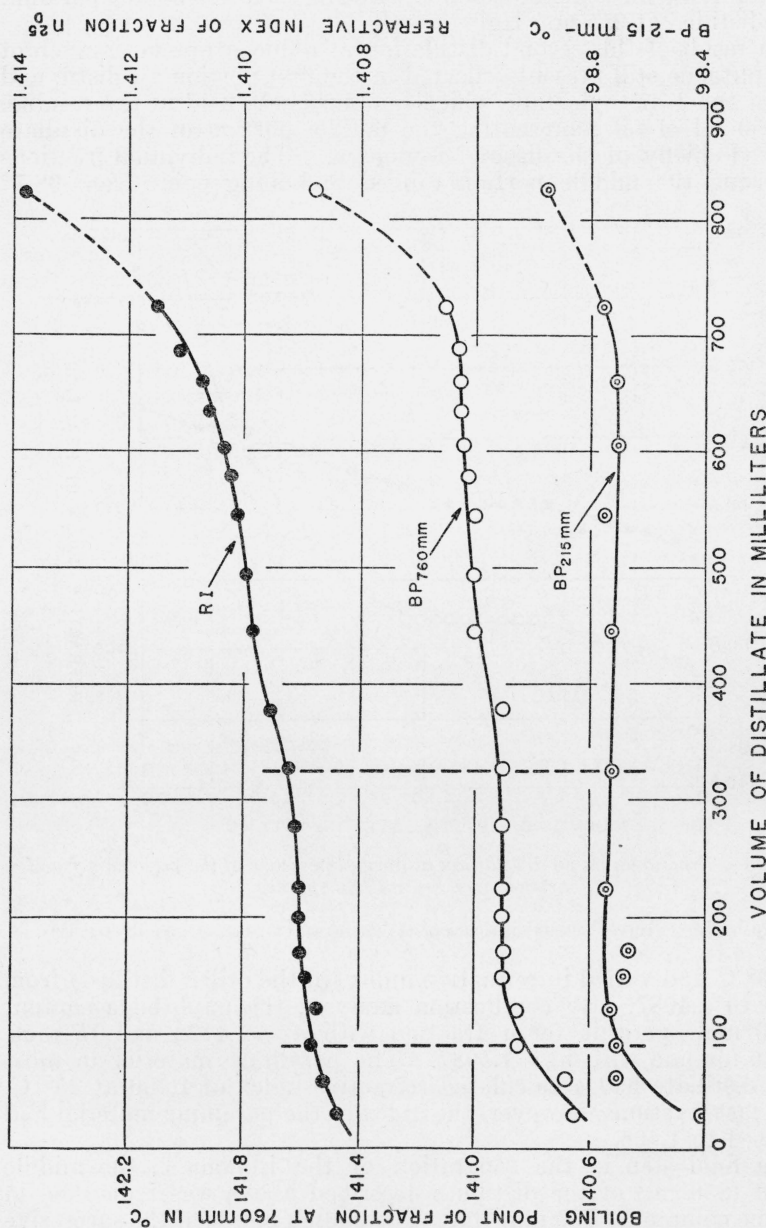


FIGURE 9.—Final fractionation by distillation of the 2,3-dimethylheptane concentrate. Top curve, refractive indices; middle curve, boiling points at 760 mm Hg; and bottom curve, boiling points at 215 mm Hg of successive fractions. The vertical dotted lines bound the portion of the distillate later subjected to fractional crystallization.

distillate, together with the divergence of the boiling-point curves, shown by the steady increase in boiling point at 760 mm Hg (middle curve) and the steady decrease in boiling point of the fractions when

measured at 215 mm Hg (bottom curve), is regarded as substantial evidence that the major portion of the distillate was composed of a binary mixture of the unidentified nonane and 1,2,4-trimethylcyclohexane.

Although the mean refractive index of the material, 1.4095, signified that the isononane was the chief constituent, none of the distillation fractions would freeze. A 240-ml portion, characterized by a constant boiling point of 140.9° C and a constant refractive index of 1.4090, was subjected to a fractional crystallization from its solution in propane and methane [13]. Apparently a crystalline phase formed, but when separated and freed from solvent it had the same physical properties as the oil in the mother liquid, indicating that no fractionation had taken place.<sup>13</sup>

### VIII. PROPERTIES OF THE ISOMERIC NONANE FRACTION AND THE PROBABLE IDENTITY OF THE NONANE WITH 2,3-DIMETHYLHEPTANE

The properties of the recombined material from the crystallization experiment are as follows: Boiling point at 760 mm Hg, 140.80° C; congeals to a glass at -119° C; density at 20° C, 0.7340 g/ml; refractive index,  $n_D^{20} = 1.4121$ ; critical solution temperature in aniline, 71° C. From two determinations by combustion, the ratio of moles of H<sub>2</sub>O to moles of CO<sub>2</sub> was found to be  $1.0950 \pm 0.0002$ . From this it was estimated that the petroleum fraction contained 85.5 mole percent of the nonane and 14.5 mole percent of 1,2,4-trimethylcyclohexane.

The properties of the constituent isononane, calculated from those of the petroleum fraction by correcting for the effect of the 1,2,4-trimethylcyclohexane present, are given in table 3. That the compound is related to, if not identical with 2,3-dimethylheptane, is indicated in the table by the similarity in their physical properties. Of the 16 isomeric nonanes which have been prepared (chiefly the substituted octanes and heptanes) 2,3-dimethylheptane is the only one which has properties similar to those of the petroleum hydrocarbon. However, in the absence of specific information concerning the properties of other possible isomers of nonane, it cannot be stated definitely that the two compounds are identical. General knowledge relating the properties of paraffin hydrocarbons to their molecular structure [15] indicates that only a few of the 19 unreported nonanes can be closely related to the nonane in question. From such a correlation, all of the trimethylhexanes and tetramethylpentanes may be expected to boil below 140° C and all of the dimethylethylpentanes may be expected to have densities greater than that of the isolated hydrocarbon. Some of the methylethylhexanes, however, as well as some of the dimethylheptanes, can be expected to have properties similar in magnitude to those of the nonane from petroleum. These include, 3,5-, 3,4-, and 4,4-dimethylheptane and 3,3-, and 3,4- methylethylhexane.

<sup>13</sup> A method was considered for purifying the material by dehydrogenation of the naphthene present, followed by adsorption of the aromatic product, but time was not available to make an adequate study of its possibilities.



TABLE 3.—Comparison of the properties of an isomeric nonane from petroleum with those of 2,3-dimethylheptane

Nonane, C <sub>9</sub> H <sub>20</sub>	Boiling point (760 mm Hg)	Behavior on cooling	Density at 20° C	Refractive index
Petroleum fraction, corrected for naphthene content.....	° C 140.7	° C -----	g/ml 0.727	n <sub>D</sub> <sup>20</sup> 1.4095
2,3-Dimethylheptane, Whitmore and Southgate <sup>a</sup> .....	140.65	glass at -116.7	.7235	1.4085

<sup>a</sup> Private communication from F. C. Whitmore and H. A. Southgate, Pennsylvania State College.

<sup>b</sup> Initial boiling point.  $dp/dt=0.049$ .

## IX. CONTENT OF 1,2,4-TRIMETHYLCYCLOHEXANE AND THE ISONONANE IN THE PETROLEUM

Of the 3 liters of petroleum shown in figure 2 to boil between 98° and 99° C at 215 mm Hg, nearly 2 liters was 1,2,4-trimethylcyclohexane and somewhat less than a liter was the isomeric nonane. It is estimated that the percentage of 1,2,4-trimethylcyclohexane in the petroleum is about 0.1, and that of the isononane about 0.05, by volume.<sup>14</sup>

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<sup>14</sup> See references [16, 17] for a discussion as to the accuracy of these estimates.