U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1296

Part of Journal of Research of the National Bureau of Standards, Volume 24, May 1940

ISOLATION OF 3-METHYLHEXANE, *trans*-1,2-DIMETHYLCYCLOPENTANE, AND *trans*-1,3-DIMETHYLCYCLOPENTANE FROM PETROLEUM* [1]

By Augustus R. Glasgow, Jr.[2]

ABSTRACT

The fraction of a midcontinent petroleum boiling between 90° and 92° C, from which the aromatic hydrocarbons previously had been removed, was substantially resolved into its constituent hydrocarbons. Alternation of atmospheric distillation and azeotropic distillation with methyl alcohol separated the material boiling between 90° and 91.2° C into a paraffinic concentrate, containing approximately 75 percent of 2-methylhexane, and a naphthenic concentrate. From the naphthenic concentrate, *trans*-1,3-dimethylcyclopentane was isolated by crystallization from liquid ethane. A similar procedure separated the material boiling between 91.2° and 92° C into a naphthenic and a paraffinic concentrate. From the naphthenic concentrate, *trans*-1,2-dimethylcyclopentane was isolated by crystallization from liquid propane plus methane. From the paraffinic concentrate, 3-methylhexane was obtained in the residue from distillations at reduced pressure (215 mm Hg).

The boiling point, refractive index, freezing point, density, carbon-hydrogen ratio, and critical solution temperature in aniline were determined for the three hydrocarbons. Referred to the content of *n*-heptane as unity, the relative amounts of the three hydrocarbons in this petroleum were estimated to be as follows: *trans*-1,3-dimethylcyclopentane, 0.21; 3-methylhexane, 0.25; *trans*-1,2-dimethylcyclopentane, 0.31.

CONTENTS

I. INTRODUCTION

The presence of "isoheptane" and "dimethylcyclopentane" in the fraction of petroleum normally boiling between 87° and 98° C has been reported by many investigators, but, except for the work done previously in this laboratory by Bruun and Hicks-Bruun [1, 2],[3] no

* Presented before the Division of Petroleum Chemistry of the American Chemical Society at the meeting in Cincinnati, Ohio; April 8–12, 1940.

[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received.

[2] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

[3] Figures in brackets indicate the literature references at the end of this paper.

one has actually separated the material into any of its constituent hydrocarbons. Most previous workers [4 to 11] have considered the "isoheptane" fraction to be 2-methylhexane or have reported that although the isoheptanes were present in considerable quantity, their separation by physical means was difficult or impossible. The "dimethylcyclopentane" fraction has been regarded as 1,3-dimethylcyclopentane, or the identification has been left incomplete.

Bruun and Hicks-Bruun [1], working with the "isoheptane" fraction of petroleum in this laboratory, isolated 2-methylhexane from the distillate boiling between 90° and 91° C. On treating the distillate boiling at 91.8° C, with chlorosulfonic acid, they obtained some hydrocarbon material that boiled at 91.9° C and had a refractive index of 1.3912 at 20° C [2]. From a comparison of the constants of this material with those of pure compounds, Bruun and Hicks-Bruun [2] concluded that the paraffin in the distillate at 91.8° C was most probably 3-methylhexane rather than a mixture of 2-methylhexane and 3-ethylpentane, which combination was next most probable.

In 1896, Zelinsky and Rudsky [12] synthesized 1,3-dimethylcyclopentane and reported the following properties: bp_{760}, 91° to 93° C; d_4^{20}, 0.7543. Markownikoff [13] believed that some material which he isolated from Caucasian petroleum was identical with the 1,3-dimethylcyclopentane synthesized by Zelinsky and Rudsky [12]. His material boiled normally between 91° and 93° C and had a specific gravity, d_4^{20}, 0.7321.

Mabery and Sieplein [14] found they could substitute one atom of bromine in a petroleum fraction boiling at 98° to 100° C (which contained methylcyclohexane) and two atoms of bromine in the fraction 96° to 98° C. From the fraction so treated, they obtained a compound with the formula $C_7H_{12}Br_2$, which they believed to have been formed from dimethylcyclopentane.

Balbiano and Zeppa [15] oxidized with nitric acid a petroleum fraction which distilled between 87° and 92° C, and obtained a mixture of 1,4-*p*-nitrobenzoic acid, nitrobenzene, adipic acid, succinic acid, and acetic acid. The 1,4-*p*-nitrobenzoic acid was assumed to be proof of the presence of 1,3-dimethylcyclopentane in the petroleum.

By distilling cracked distillates of petroleum with aniline, Brame and Hunter [11] isolated some naphthenic material which had the constants: bp_{760}, 93° to 94° C; d_4^{20}, 0.7648; n_D^{20}, 1.4110. This material was identified as a dimethylcyclopentane because its properties agreed with those of a synthetic dimethylcyclopentane, the constants of which were: bp_{760}, 93° C; d_4^{20}, 0.7530; n_D^{20}, 1.4130.

The present paper reports the completion of the work begun by Bruun and Hicks-Bruun [1, 2] on the resolution of that fraction of petroleum normally boiling between 87° and 98° C. There are described here the isolation and identification of 3-methylhexane, *trans*-1,2-dimethylcyclopentane, and *trans*-1,3-dimethylcyclopentane from the fraction normally boiling between 90° and 92° C.

II. TREATMENT OF THE MATERIAL PRIOR TO THE PRESENT INVESTIGATION

In the work by Bruun and Hicks-Bruun [1, 2, 3] on the fraction of petroleum normally boiling between 87° and 98° C, the material was subjected to several processes of fractionation. The toluene was

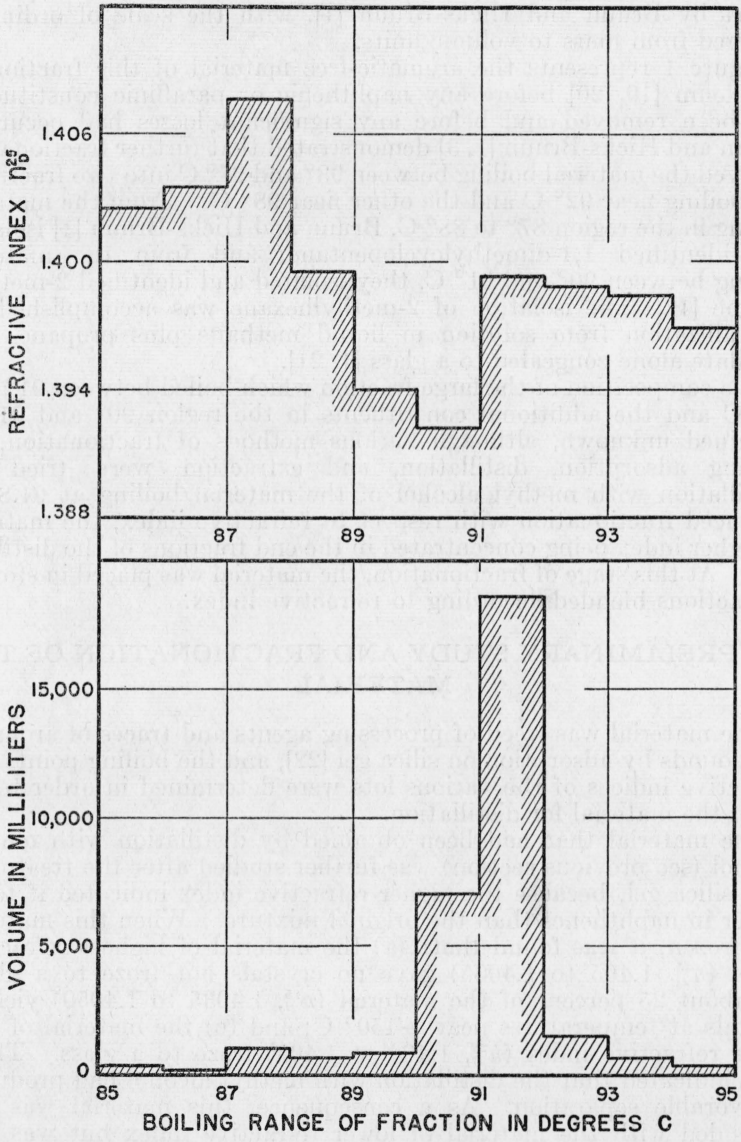

FIGURE 1.—*Volumes and refractive indices of the fractions boiling between 85° and 95° C at 760 mm* Hg, *after removal of aromatic hydrocarbons and subsequent distillation.*

The scale of ordinates in the lower graph gives the volume in milliliters and in the upper graph the refractive indices for fractions of 1° C boiling range, as indicated. The scale of abscissae gives the boiling range of the fractions in degrees centigrade.

removed by nitration [17], and the material which remained was distilled in an 11–m jack-chain column [18]. The distribution by volume of the material with respect to the boiling point and refractive index at this stage is shown in figure 1, which is reproduced from the

report by Bruun and Hicks-Bruun [1], with the scale of ordinates changed from mass to volume units.

Figure 1 represents the aromatic-free material of this fraction of petroleum [19, 20] before any naphthenic or paraffinic constituents had been removed and before any significant losses had occurred. Bruun and Hicks-Bruun [1, 3] demonstrated that further fractionation resolved the material boiling between 93° and 97° C into two fractions, one boiling near 92° C and the other near 98° C. From the material boiling in the region 87° to 88° C, Bruun and Hicks-Bruun [1] isolated and identified 1,1-dimethylcyclopentane; and from the material boiling between 90° and 91° C, they isolated and identified 2-methylhexane [1]. The isolation of 2-methylhexane was accomplished by crystallization from solution in liquid methane plus propane—the distillate alone congealed to a glass [1, 21].

The composition of the large fraction which boiled between 91° and 92° C and the additional constituents in the region 90° and 91° C remained unknown, although various methods of fractionation, including adsorption, distillation, and extraction, were tried [2]. Distillation with methyl alcohol of the material boiling at 91.8° C produced fractionation with respect to refractive index, the material of higher index being concentrated in the end fractions of the distillate [24]. At this stage of fractionation, the material was placed in storage in fractions blended according to refractive index.

III. PRELIMINARY STUDY AND FRACTIONATION OF THE MATERIAL

The material was freed of processing agents and traces of aromatic compounds by adsorption on silica gel [22], and the boiling points and refractive indices of the various lots were determined in order to reblend the material for distillation.

The material that had been obtained by distillation with methyl alcohol (see previous section) was further studied after the treatment with silica gel, because the higher refractive index indicated it to be higher in naphthenes than the original mixture. When this material was frozen, it was found that: (a) the material of highest refractive index (n_D^{25}, 1.405 to 1.4065) gave no crystals but froze to a glass; (b) about 25 percent of the material (n_D^{25}, 1.4035 to 1.4050) yielded crystals at temperatures near −150° C; and (c) the material of still lower refractive index (n_D^{25}, 1.400 to 1.403) froze to a glass. These facts indicated that the distillation with methyl alcohol had produced a favorable separation. As a consequence, this material was not reblended with the material of lower refractive index but was distilled separately at atmospheric pressure. This distillation removed some higher-boiling material, after which all of the material that had a refractive index greater than 1.4035 at 25° C crystallized on cooling.

The material boiling between 90° and 92° C was systematically distilled through columns [4] packed with single-turn stainless-steel helices. These distillations removed material that boiled higher or lower than the range under investigation (bp_{760}, 90° to 92.2° C), and served to realine the material with respect to normal distillation behavior. The result of this realinement is shown in figure 2.

[4] When tested with a known mixture of *n*-heptane and methylcyclohexane, these columns were calculated to have a separating efficiency of about 95 theoretical plates.

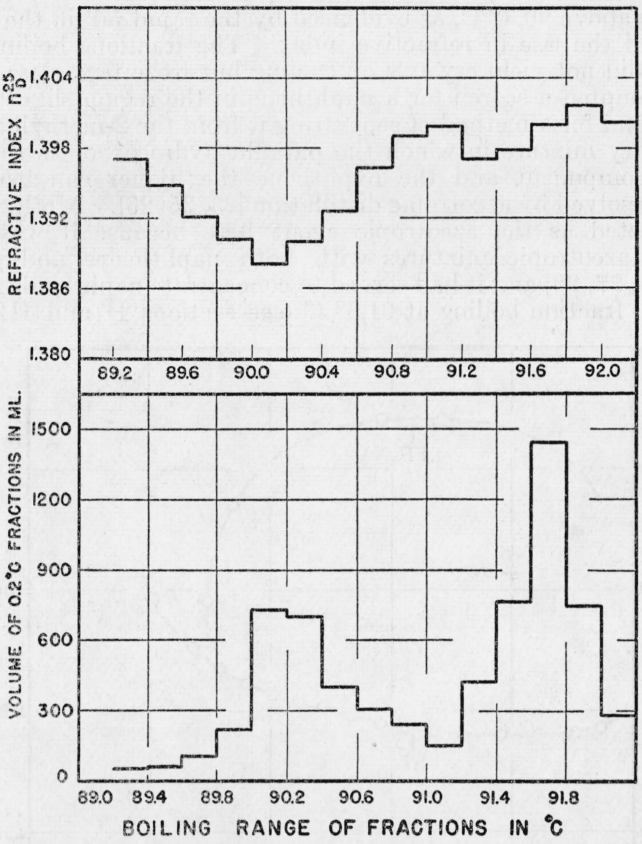

FIGURE 2.—*Volumes and refractive indices of the aromatic-free fractions boiling between 89.2° and 92.2° C.*

The scale of ordinates in the lower graph gives the volumes in milliliters and in the upper graph the refractive indices, from fractions of 0.2° C boiling range, as indicated. The scale of abscissae gives the boiling range of the fractions in 0.2° C.

IV. RESOLUTION OF THE MATERIAL BOILING BETWEEN 90° AND 91.2° C INTO CONCENTRATES OF 2-METHYLHEXANE AND *trans*-1,3-DIMETHYLCYCLOPENTANE

A study of the distribution of the material with respect to boiling point and refractive index (shown in figure 2) revealed that: (a) naphthenic material (presumably 1,1-dimethylcyclopentane [1]) was concentrating below 90° C; (b) paraffinic material (presumably 2-methylhexane [1]) was concentrating in the region 90° to 91.2° C; and (c) the volume of distillate dropped to a minimum at 91.2° C, with increasing naphthenic content. The material boiling from 90° to 91.2° C, therefore, contained 2-methylhexane and higher-boiling naphthenes.

Correlation of the freezing behavior, boiling points, and refractive indices of fractions of the distillate, shown in figure 3, indicated that: (a) the material in the region 90° to 90.3° C was mainly 2-methylhexane; and (b) the distillate became enriched in naphthenic con-

stituents above 90.3° C, as evidenced by the rapid fall in the freezing point and the rise in refractive index. The fractions boiling above 90.5° C did not yield crystals on cooling but froze to a glass. These facts prompted a search for a naphthene in the region slightly above 90.5° C and for a method of separating it from the 2-methylhexane.

A binary mixture in which the paraffin hydrocarbon is the lower-boiling component and the naphthene the higher can usually be readily resolved by azeotropic distillation [23, 25, 26]. Methyl alcohol was selected as the azeotropic agent here because it was known to form azeotropic mixtures with both naphthenes and paraffins [11, 3, 24, 27, 28] and it had served to concentrate naphthenic material from the fraction boiling at 91.8° C (see sections II and III). The

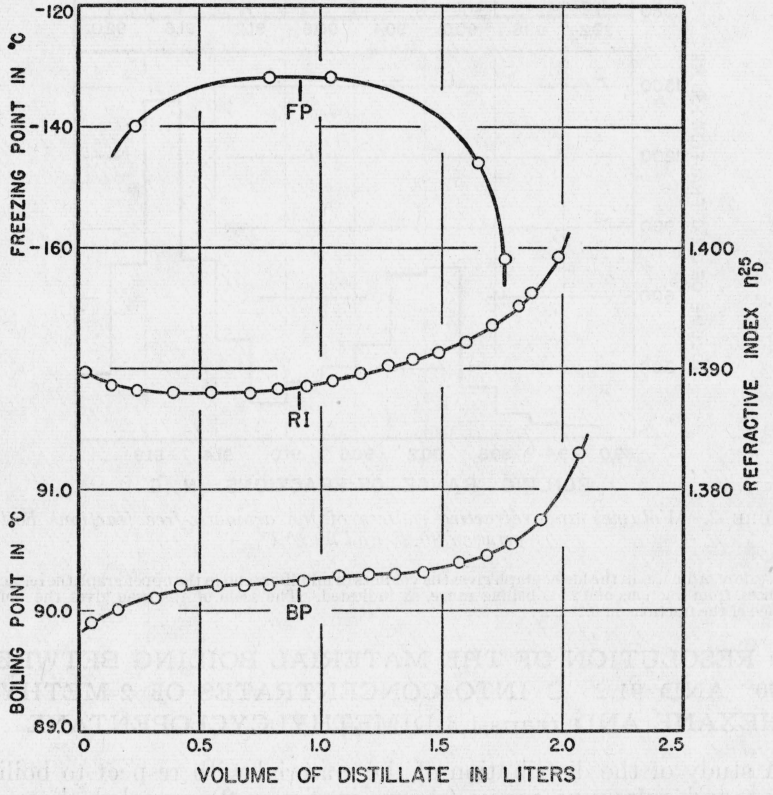

FIGURE 3.—*Fractionation, by distillation at 760 mm* Hg, *of material boiling between 90° and 90.8° C.*

The scale of ordinates in the figure gives the freezing points (upper left), the boiling points (lower left), and the refractive indices (middle right), for the various fractions. The scale of abscissae gives the volume of the distillate in liters.

material boiling between 90° and 91.2° C, which on the basis of refractive index, boiling point, and freezing behavior was deduced to be essentially a mixture of a lower-boiling paraffin and higher-boiling naphthenes, was accordingly processed by azeotropic distillation with methyl alcohol. A liter of this material was first distilled at atmospheric pressure, and then redistilled with twice its volume of methyl alcohol in an azeotropic distillation. In figure 4 are shown the

results of the two distillations, with the boiling points of the fractions of oil from the normal distillation being compared with the boiling points of the fractions of oil obtained from the azeotropic distillation. The properties of the oil from the two distillations show that the separation by azeotropic distillation was far more efficient. The azeotropic distillates had boiling points of 57.0° and 57.45° C for the first and last fractions, respectively. The ratio of oil to alcohol was about 6 to 4 throughout. Though the total boiling range of the azeotropic fractions was slightly less than the total boiling range of the material when distilled as oil, the azeotropic distillation gave a

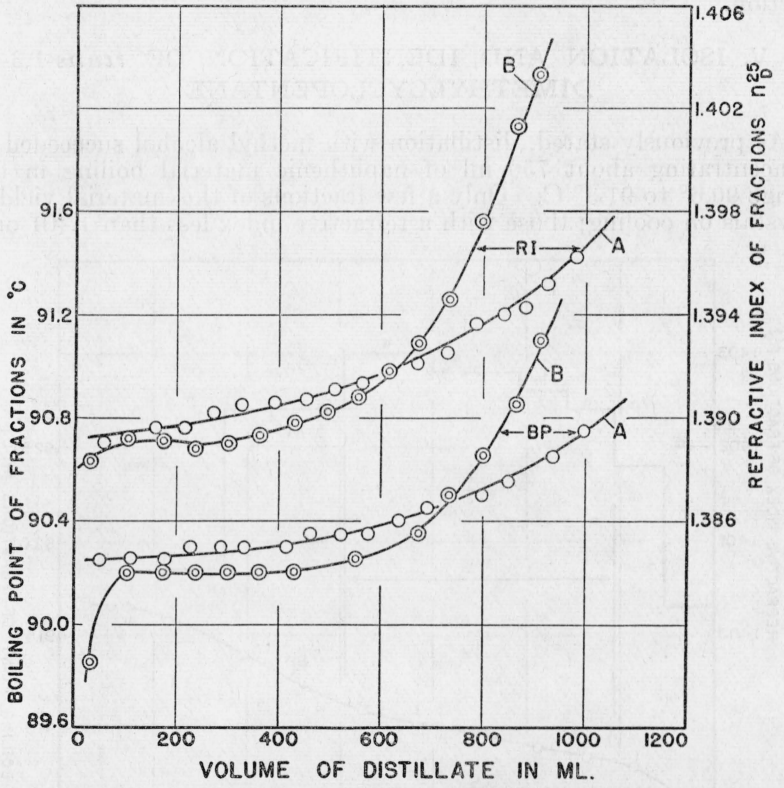

FIGURE 4.—*Fractionation of the paraffin-naphthene mixture by distillation at normal pressure is contrasted to the fractionation of the oil by azeotropic distillation with methyl alcohol.*

The curves marked *A* refer to the oil fractions from the normal distillation and the curves marked *B* refer to the oil fractions obtained from the azeotropic distillation. The scale of ordinates in the figure gives on the left the boiling points and on the right the refractive indices for the oil fractions from the two distillations. The scale of abscissae gives the volume of the oil in milliliters.

far better separation because of a more favorable relation between the liquid and vapor phases in the azeotropic system [23]. Similar behavior has been found in azeotropic distillations of other oil fractions with acetic acid [25, 26].

Further processing of the material boiling between 90° and 91.2° C by distillation with methyl alcohol and distillation as oil at normal pressure resolved this material into over 1½ liters of a paraffinic concentrate and ¾ liter of a naphthenic concentrate. It was calculated

that the paraffinic concentrate contained about 75 percent of 2-methylhexane, on the basis of the following properties: bp_{760}, 90.0° to 90.2° C; n_D^{25}, 1.387 to 1.388, fp(entire lot),—130° C. The naphthenic concentrate had the following properties: bp_{760}, 90.6° to 91.3° C; n_D^{25}, 1.395 to 1.402. A few of the fractions of higher refractive index from the naphthenic concentrate gave freezing points near —150° C. Since this was the first time distillate in this region was sufficiently enriched in a naphthene to crystallize on cooling, a program was outlined to isolate this constituent by fractional crystallization. The separation and identification of this naphthene are described in the following section.

V. ISOLATION AND IDENTIFICATION OF *trans*-1,3-DIMETHYLCYCLOPENTANE

As previously stated, distillation with methyl alcohol succeeded in concentrating about 750 ml of naphthenic material boiling in the range 90.6° to 91.3° C. Only a few fractions of this material yielded crystals on cooling; those with a refractive index less than 1.401 or a

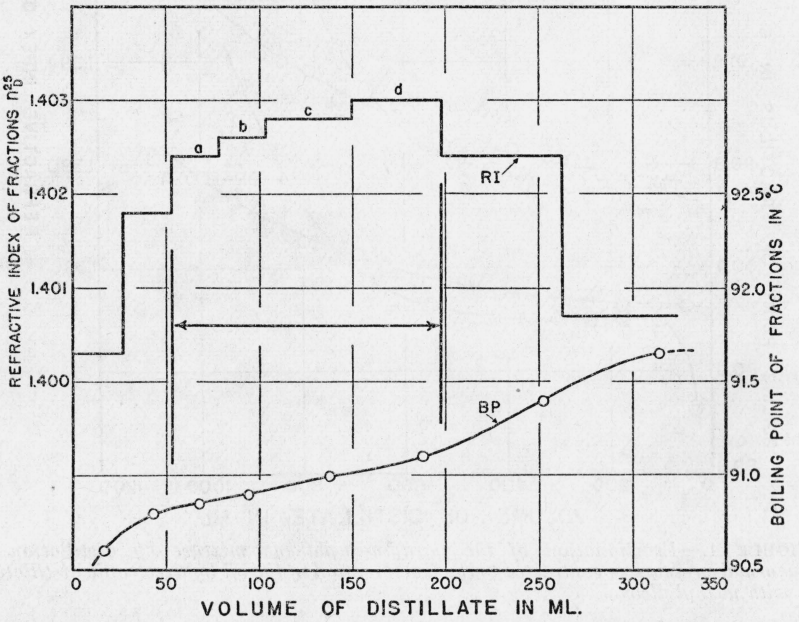

FIGURE 5.—*Final distillation at 760 mm* Hg *of the best concentrate of trans-1,3-dimethylcyclopentane.*

The scale of ordinates gives on the right the boiling points and on the left the refractive indices for the various distillate fractions. The scale of abscissae gives the volume in milliliters. The letters above the curve of refractive index refer to melting points. The arrow indicates the region of distillate that yielded crystals on cooling.

boiling point greater than 91.2° C did not. In order to obtain a sufficient quantity of material for the process of fractional crystallization, the material was further fractionated by azeotropic distillation. This process yielded 350 ml of material which crystallized and which had the following properties: bp_{760}, 90.7° to 91.2° C; n_D^{25}, 1.401 to

1.403; fp, about −150° C. This fraction was distilled at atmospheric pressure to remove any higher- or lower-boiling constituents and to further concentrate the naphthene.

The result of this distillation is shown in figure 5. The portion of the distillate marked by the arrows crystallized, while above and below these limits the distillate congealed to a glass. The letters above the curve of refractive index identify fractions on which determinations of melting point were made. These values were: *a* and *b* mixed, −140.55° C; *c*, −140.74° C; *d*, −141.76° C. All of these fractions were characterized by two breaks in the melting curve, the first of which was approximately the same in each.

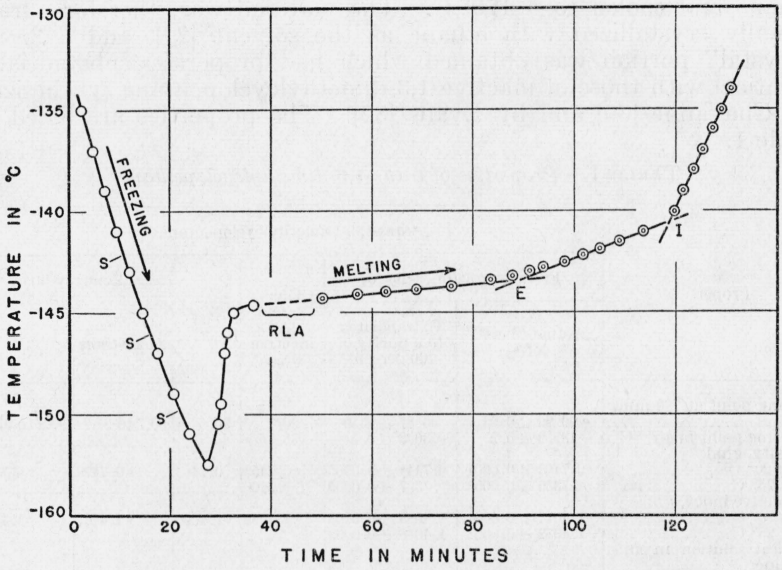

FIGURE 6.—*Time-temperature cooling and warming curves of impure trans-1,3-dimethylcyclopentane.*

The scale of ordinates gives the temperature in degrees centigrade. The scale of abscissae gives the time in minutes. The letters have the following significance: *S*, stirred with a cold rod to induce crystallization; *RLA*, changed from a cooling to warming bath; *E*, eutectic; *I*, melting point.

The cooling and melting curve of the distillate fraction, labeled *c* in figure 5, is shown in figure 6. The break in the curve, labeled *E*, indicates (at −143.5° C) the eutectic of the 1,3-dimethylcyclopentane (the naphthene isolated from this material by fractional crystallization) with an additional constituent. It is not possible to say whether the eutectic formed here is between *trans*-1,3-dimethylcyclopentane and *trans*-1,2-dimethylcyclopentane (the higher-boiling naphthene present in this fraction) or between *trans*-1,3-dimethylcyclopentane and 2-methylhexane, as a theoretical calculation of the eutectic points of the two systems yields approximately the same result. The naphthene in excess of the eutectic proportion is shown by that part of the melting curve marked *E* to *I*. From a study of the curve, it can be estimated roughly that in fractional crystallization about three-fifths of the material will be eutectic material. It is this unfavorable relationship which later made the isolation of a sample of

higher purity practically impossible, because of the small amount of material. The fractions were studied by means of melting curves rather than freezing curves, because it was observed that material close to eutectic composition became solid near the eutectic temperature and consequently the temperature of the initial freezing point of the material was never realized. This effect has been observed by others [26, 29].

The middle portion (150 ml) of the distillate shown in figure 5 was mixed for crystallization because the composition of these fractions was approximately the same, as evidenced by their melting points. From some "test tube" experiments, it was found that the material formed well-defined crystals when mixed with two volumes of liquid ethane and cooled to −170° C. The material was, therefore, fractionally crystallized with ethane as the solvent [21], and a 35-ml "crystal" portion was obtained which had properties substantially identical with those of inactive 1,3-dimethylcyclopentane synthesized by Chavanne [30] and by Evans [32]. The properties are listed in table 1.

TABLE 1.—*Properties of trans-1,3-dimethylcyclopentane*

Properties	*trans*-1, 3-Dimethylcyclopentane					
	From petroleum, Glasgow		Chavanne [30] inactive	Evans [32] inactive	Zelinsky [31]	
	Actual "best" lot [a]	Extrapolated to a purity of 100 percent			*dextro-trans*	Inactive-*trans*
Boiling point at 760 mm, °C	[b] 90.90 ±0.03	90.87 ±0.10	90.7	90.5	90.7 to 91.2[c]	90.9 to 91.4[c]
Freezing point in air, °C	−137.2 ±0.2	−136.3 ±0.5	−136.75			
Density, g/ml:						
At 20° C	0.7403 ±0.0001	0.7444 ±0.0005	[c] 0.7453	0.7463	[c] 0.7479	[c] 0.7446
At 25° C	.7356 ±0.0001	.7397 ±0.0005	[c] .7408			
Refractive index, n_D:						
At 20° C	1.4074 ±0.0001	1.4088 ±0.0003	[c] 1.4080	1.4096	[c] 1.4101	[c] 1.4084
At 25° C	1.4052 ±0.0001	1.4066 ±0.0003				
Critical solution in aniline:						
Temperature, °C	51.5 ±0.2	49.9 ±0.5	48.8	46.4		
Composition, mole fraction of hydrocarbon	0.42 ±0.02	0.42 ±0.03				
Analytical combustion, moles H_2O/moles CO_2	[d] 1.01045 ±0.00006					

[a] Impurity (presumably about 0.073 mole fraction of 3-methylhexane and the remainder trans-1, 2-dimethylcyclopentane) estimated to be 0.10 ±0.02 mole fraction.
[b] Determined by C. B. Willingham and F. D. Rossini.
[c] Corrected to the given temperature or pressure from observations made at a slightly different temperature or pressure.
[d] Mean and mean deviation of 2 experiments (see text).

Chavanne's preparation can be shown to be *trans-dl*-1,3-dimethylcyclopentane by the following reasoning, which Zelinsky [31] applied to one of his synthetic preparations: The *cis* isomer of 1,3-dimethylcyclopentane cannot exhibit optical activity, whereas the *trans* isomer can exist in three forms, two optically active forms which are mirror images of each other and an inactive form which is the *dl* mixture of these two. Zelinsky compared the properties of the *trans-dextro* form with those of an inactive form of 1,3-dimethylcyclopentane [31, 12] and concluded that the inactive form also had the methyl groups in the *trans* position.

Time-temperature cooling curves of the best lot of *trans*-1,3-dimethylcyclopentane are shown in figure 7. The two cooling curves were obtained with different rates of cooling and are in excellent accord, though they are not sufficiently complete to permit estimation of the amount of impurity.

The ratio of the number of moles of H_2O to the number of moles of CO_2 formed in combustion was determined, as described in reference [33], to be 1.01040 and 1.01051. From this it was calculated that the amount of paraffinic impurity in this material was 0.073 mole fraction, with an estimated uncertainty of ± 0.005. Because of the likelihood that this material also contained a small amount of napthenic

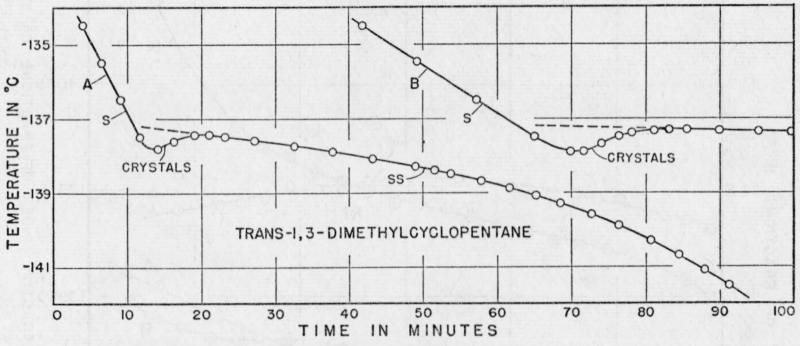

FIGURE 7.—*Time-temperature cooling curves of trans-1,3-dimethylcyclopentane.*

The scale of ordinates gives the temperature in degrees centigrade. The scale of abscissae gives the time in minutes. The letters have the following significance: *A*, *B*, cooling curves on the same sample obtained by different gradients; *S*, stirred with cold rod to induce crystallization; *SS*, stirrer stopped.

impurity, which would have the same value of carbon-hydrogen ratio as the main constituent, the amount of impurity in this best lot of *trans*-1,3-dimethylcyclopentane was estimated to be 0.10 ± 0.02 mole fraction.

VI. RESOLUTION OF THE MATERIAL BOILING BETWEEN 91.2° AND 92.2° C INTO CONCENTRATES OF *trans*-1,2-DIMETHYLCYCLOPENTANE AND 3-METHYLHEXANE

The distribution of the material boiling between 91.2° and 92.2° C with respect to boiling point and refractive index is shown in figure 2. The largest amount of material distilled between 91.6° and 91.8° C. A calculation based on the refractive index indicated that this material contained approximately 60 percent of napththenic constituents.

It was known at this stage in the investigation that *trans*-1,3-dimethylcyclopentane was present in this mixture, because it had been isolated from material which distilled between 90.8° and 91.1° C. Also, as pointed out in sections II and III of this paper, distillation with methyl alcohol served to concentrate some material of higher refractive index in the higher-boiling end. This distillate, which boiled 1° C higher than did the *trans*-1,3-dimethylcyclopentane, was assumed to be rich in a second naphthene. It was therefore concluded that, as normal distillate, the material was a mixture of at least two naphthenes and one paraffin.

All the material boiling between 91.2° and 92.2° C was systematically fractionated. Ordinary distillation was alternated with azeotropic distillation with methyl alcohol. The azeotropic distillation served to separate the two naphthenes from the paraffin, and the normal distillation resulted in a partial separation of the *trans*-1,3-dimethylcyclopentane from *trans*-1,2-dimethylcyclopentane, which was concentrated at about 91.8° C.

The results of two distillations on the same blend of this material are shown in figure 8, with the boiling points and refractive indices of the fractions from the normal distillation being compared with the

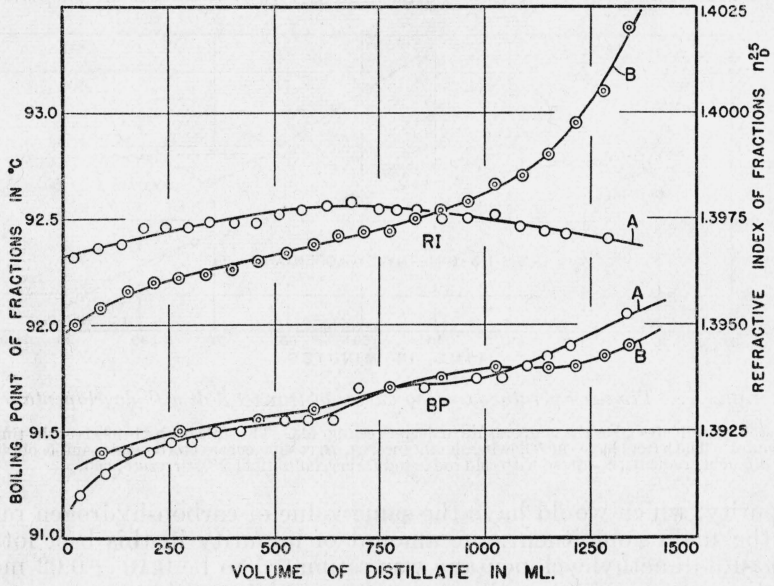

FIGURE 8.—*Fractionation of the paraffin-naphthene mixture by distillation at normal pressure is contrasted with the fractionation of the oil by azeotropic distillation with methyl alcohol.*

The curves marked *A* refer to the oil fractions from the normal distillation and the curves marked *B* refer to the oil fraction obtained from the azeotropic distillation. The scale of ordinates gives on the right the refractive indices and on the left the boiling points, for the oil fractions from the two distillations. The scale of abscissae gives the volume in milliliters.

boiling points and refractive indices of the fractions of oil from the azeotropic distillation. The properties of the oil show that the naphthenic material was concentrated in the azeotropic distillation, whereas in the normal distillation the naphthenes were distributed over the whole range. The fact that the boiling range of the oil from the two distillations was approximately the same was in accord with the previous conclusion that this material contained two naphthenes and one paraffin. In the azeotropic distillate, the ratio of oil to alcohol was approximately three to two and the minimum boiling point was 57.4° C for the material of lower refractive index and 57.65° C for that of higher index. The favorable relationship existing between the liquid and vapor phases in an azeotropic distillation produced a separation in spite of the fact that the boiling range was small.

The naphthenic concentrate obtained from the azeotropic distillation was distilled normally as oil at atmospheric pressure in order to

separate the naphthenes. The result of this distillation is shown in figure 9.

A partial resolution of *trans*-1,3-dimethylcyclopentane from the concentrate of the higher-boiling naphthene was effected by interlocking the two types of distillation. A concentrate of the unknown naphthene was prepared which was partially freed of *trans*-1,3-dimethylcyclopentane. The isolation of this naphthene, which was later identified as *trans*-1,2-dimethylcyclopentane, is described in the following section.

In a like manner, a paraffinic concentrate was obtained by exhaustive distillation with methyl alcohol followed by distillation of the oil portion of the azeotropic distillate at atmospheric pressure. The

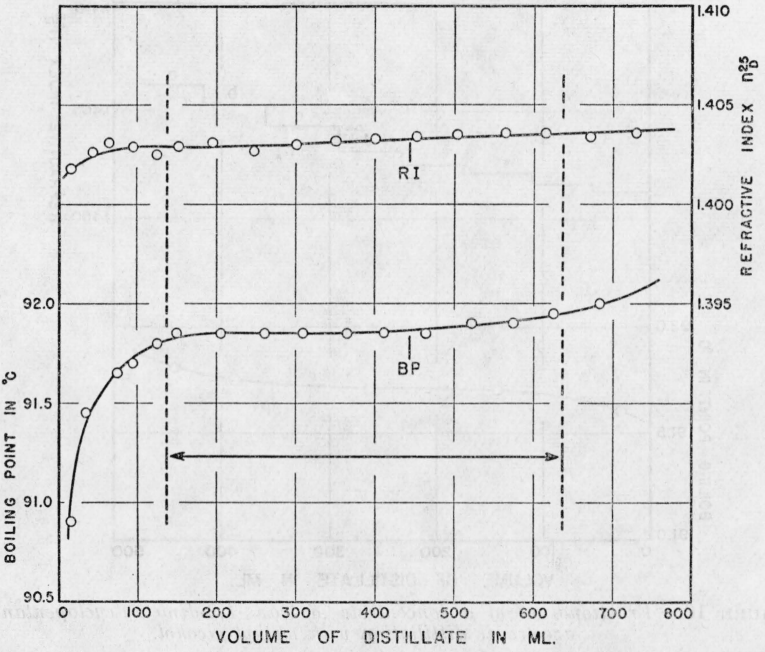

FIGURE 9.—*Fractionation of a concentrate of trans-1,2-dimethylcyclopentane by distillation at normal pressure.*

The scale of ordinates gives on the right the refractive indices and on the left the boiling points of the distillate fractions. The scale of abscissae gives the volume of distillate in milliliters. The region marked by the arrow was redistilled, see figure 10.

azeotropic distillation served to remove naphthenes and concentrate the paraffin. The normal distillation removed some 1,3-dimethylcyclopentane and lower-boiling material. By this process, about a liter of paraffinic concentrate was obtained which distilled between 91.4° and 91.8° C. It was calculated, on the basis of refractive index, that this material was approximately 50 percent paraffinic. This was the stock from which 3-methylhexane was subsequently isolated (see section VIII).

222120—40——3

VII. ISOLATION AND IDENTIFICATION OF *trans*-1,2-DIMETHYLCYCLOPENTANE

The 0.5 liter of naphthenic material (indicated in figure 9) was redistilled with methyl alcohol to fractionate it further with respect to refractive index. The properties of the oil portion of the azeotropic distillate are shown in figure 10. The letters over the refractive-index curve refer to fractions for which values of the freezing point were determined. These were: *a*, −132.5° C; *b*, −137° C; *c*, −142.5° C; *d*, −155° C. The fractions in the unlettered region contained too little of this naphthene to give crystals, and congealed to a glass on cooling. The rapid change in freezing points indicates that

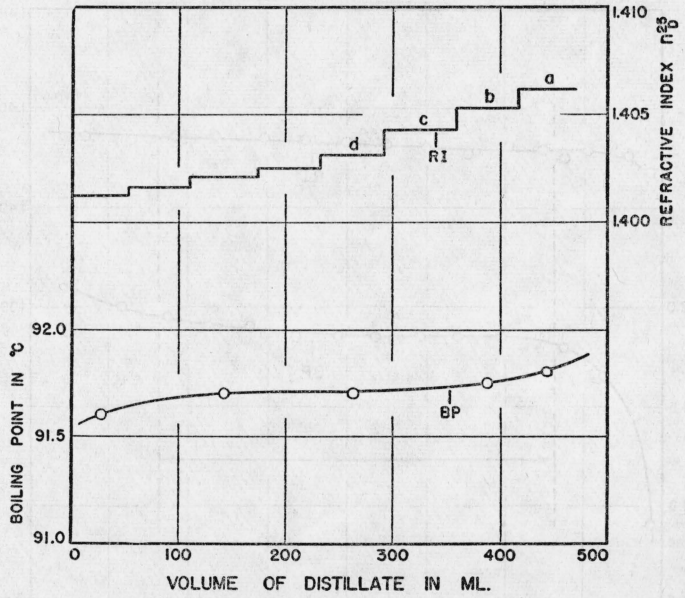

FIGURE 10.—*Fractionation of a concentrate of trans-1,2-dimethylcyclopentane by azeotropic distillation with methyl alcohol.*

The scale of ordinates gives on the left the boiling points and on the right the refractive indices of the oil portions of the azeotropic distillate. The abscissae give the volume of oil in milliliters. The letters over the curve of refractive index refer to freezing points.

the system is a ternary one, and, further, that the naphthene in question is concentrating in the end fractions of this distillation. The difficulty of freezing the first 60 percent of the distillate is attributed to the presence of the other naphthene, *trans*-1,3-dimethylcyclopentane.

The distillate was further investigated as to its fractionation by crystallization. It was found that the portion of the distillate which gave freezing points yielded nice crystals on cooling 1 volume of oil in a mixture of 1 volume of propane and 3 volumes of methane [21]. These fractions were systematically crystallized from this solvent, and the "crystal" and mother-liquor portions obtained on centrifuging were analyzed to determine what separation had occurred. The "crystal" portions from fractions *a* and *b* gave freezing points about

5° C higher than the original material, whereas for fractions *c* and *d* there was little or no difference between the freezing point of the "crystal" portion and that of the original fraction. The lower-freezing material failed to improve on crystallization, because its composition was close to that of a eutectic mixture. The "crystal" portions from fractions *a* and *b* were blended and recrystallized. The properties of the recrystallized material (bp_{760}, 92.0° C; fp, −127° C; and n_D^{25}, 1.4075) indicated it to be impure *trans*-1,2-dimethylcyclopentane. The mother liquors from these crystallizations had boiling points as low as 91.4° C and were enriched in the lower-boiling naphthene, *trans*-1,3-dimethylcyclopentane.

In order to prepare a purer sample of *trans*-1,2-dimethylcyclopentane, material with lower refractive index and poor freezing behavior was further processed by alternate distillations, as outlined in the previous section. In this way, 200 ml of naphthenic material was obtained which had the following properties: n_D^{25}, 1.406 to 1.407; fp, −127° to −135° C; bp_{760}, 91.8° to 92° C. Systematic fractional crystallization of this yielded finally a 50-ml crystal fraction of substantially pure *trans*-1,2-dimethylcyclopentane. The physical properties of this material are given in table 2. Excellent accord is observed between the properties of the material from petroleum and the synthetic material prepared by Chiurdoglu [35].

TABLE 2.—*Properties of trans-1,2-dimethylcyclopentane*

Properties	*trans*-1,2-Dimethylcyclopentane			
	From petroleum, Glasgow		Chuirdoglu [35]	Chavanne [34]
	Actual "best" lot [a]	Extrapolated to purity of 100 percent		
Boiling point at 760 mm Hg, °C	[b] 91.89±0.01	91.89±0.02	91.78	91.8±0.1
Freezing point in air, °C	−119.75±0.10	−119.25±0.15	−119	−120
Density, g/ml:				
At 20° C	0.7506±0.0001	0.7519±0.0003	0.7513_7	0.7495
At 25° C	.7460±0.0001	.7473±0.0003	[c] $.7469_1$	
Refractive index, n_D:				
At 20° C	1.4115±0.0001	1.4120±0.0001	[c] 1.4121	1.4126
At 25° C	1.4092±0.0001	1.4097±0.0001		
Critical solution in aniline:				
Temperature, °C	47.1±0.2	46.7±0.3	47.0	
Composition, mole fraction of hydrocarbon	0.52±0.03	0.52±0.03		
Analytical combustion, moles H_2O/moles CO_2	[d] 1.0029±0.0004			

[a] Impurity (presumably 3-methylhexane) estimated to be 0.020 ±0.004 mole fraction.
[b] Determined by C. B. Willingham and F. D. Rossini.
[c] Corrected to the given temperature or wavelength from observations made at a slightly different temperature or wavelength.
[d] Mean and mean deviation of 2 experiments (see text).

Time-temperature cooling and melting curves of the best lot of *trans*-1,2-dimethylcyclopentane are shown in figure 11. From these curves, the amount of liquid-soluble, solid-insoluble impurity was estimated [16] to be 0.016 ±0.004 mole fraction.[5]

[5] The value 1,540 cal/mole was used for the heat of fusion [36]. Recent unpublished work [45] indicates that the uncertainty assigned to this value may be appreciably greater than that given.

Two determinations of the ratio of the number of moles of H_2O to the number of moles of CO_2 formed in combustion [33] yielded the values 1.0032 and 1.00255. From these data, the amount of paraffinic material was calculated to be 0.020 $\pm$0.004 mole fraction.

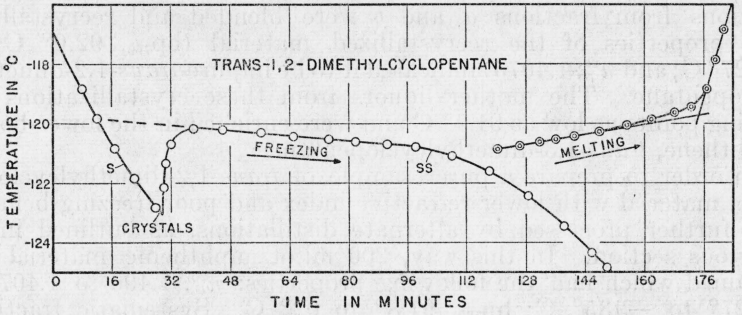

FIGURE 11.—*Time-temperature cooling and warming curves of trans-1,2-dimethylcyclopentane.*

The scale of ordinates gives the temperature in degrees centigrade. The scale of the abscissae gives the time in minutes. The letters have the following significance: *S*, stirred with a cold rod to induce crystallization; *SS*, stirrer stopped.

VIII. ISOLATION AND IDENTIFICATION OF 3-METHYLHEXANE

Alternate normal distillation and azeotropic distillation with methyl alcohol of the material boiling between 91.2° and 92.2° C produced a concentrate that was about 55 percent paraffinic.

The fact that a change in pressure sometimes produces a favorable advantage in separation [37, 38] prompted a study of the change in boiling point, between 760- and 215-mm pressure, of the naphthenic and paraffinic constituents in this fraction. The difference in boiling temperature between the two pressures was found to be 37.4° C for the paraffinic constituents and 38.5° C for the naphthenic constituents. These values were determined from the boiling points taken at the two pressures on samples of naphthenic and paraffinic concentrates in this region. A correction was applied for the content of paraffin and naphthene in the naphthenic and paraffinic samples, respectively, to arrive at this value for the difference in boiling points. The results of these measurements showed that distillation of the paraffinic concentrate at a pressure of 215 mm Hg should produce an increased fractionation because of the favorable displacement (approximately 1° C lower) of the boiling point of the naphthene with respect to that of the paraffin. Consequently, a concentrate of the paraffin that showed little resolution when distilled normally at atmospheric pressure or with methyl alcohol in an azeotropic distillation was redistilled alone at the reduced pressure. The stills used for all of this work had a separation efficiency of approximately 95 theoretical plates.

The effective separations obtained in the azeotropic and reduced pressure distillations are shown in figure 12. It is apparent from the upper half of the figure that little resolution occurred when this particular concentrate was distilled with methyl alcohol. From data obtained later, this material was estimated to be about one-half

3-methylhexane and about one-fourth each of *trans*-1,2-dimethylcyclopentane and *trans*-1,3-dimethylcyclopentane. In the lower half of figure 12, the properties of the distillate show that a very effective separation of the paraffin and the naphthenes had occurred in the

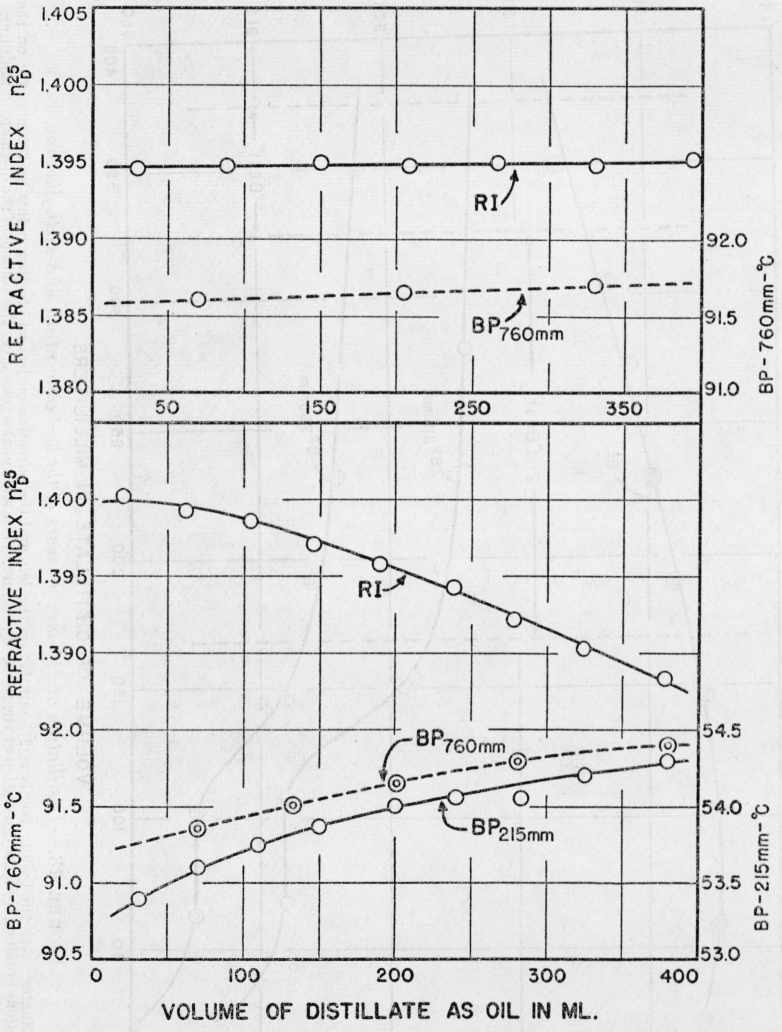

FIGURE 12.—*Fractionation of the concentrate of 3-methylhexane by azeotropic distillation contrasted to that obtained by distillation at 215 mm* Hg.

The upper half of the figure refers to the oil fractions from the azeotropic distillation and the lower half to those from the distillation at 215 mm Hg. The scale of ordinates in the upper figure gives on the left the refractive indices and on the right the boiling points. The scale of ordinates in the lower figure gives on the right the boiling points as distillate (215 mm) and on the left the refractive indices and the boiling points determined at 760 mm. The scale of abscissae gives the volume of oil in milliliters.

distillation at the reduced pressure. A calculation on the basis of refractive index showed that the initial fractions with indices as high as n_D^{25} 1.400 were about 65 percent naphthenic and that the residue was approximately 85 percent paraffinic. In fact, the properties of

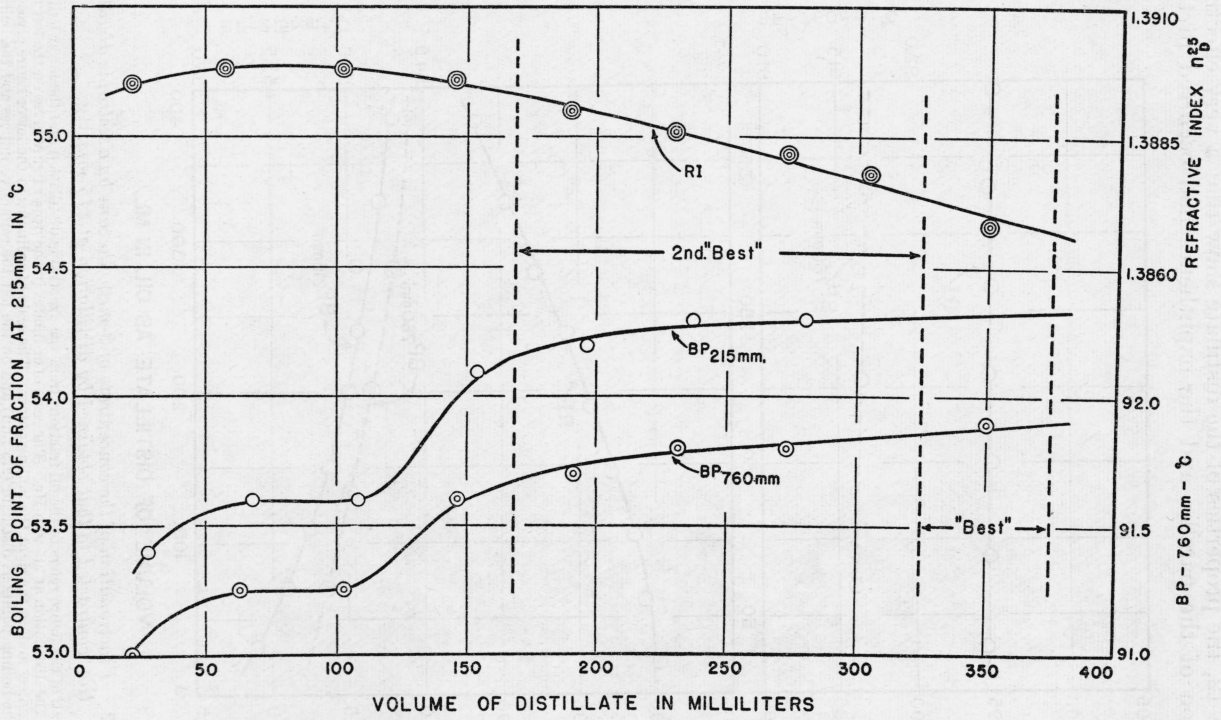

FIGURE 13.—*Distillation at 215-mm pressure of the best concentrate of 3-methylhexane.*

The scale of ordinates gives the boiling points at 215 mm Hg on the left and the refractive indices and boiling points at 760 mm Hg on the right for the fractions obtained from the distillation at the reduced pressure. The scale of abscissae gives the volume of the distillate in milliliters.

this residue, when corrected for naphthenic content, agreed well with those reported for synthetic 3-methylhexane.

The upper half of the figure refers to the oil fractions from the azeotropic distillation and the lower half to those from the distillation at 215 mm Hg. The scale of ordinates in the upper figure gives on the left the refractive indices and on the right the boiling points. The scale of ordinates in the lower figure gives on the right the boiling points as distillate (215 mm) and on the left the refractive indices and the boiling points determined at 760 mm. The scale of abscissae gives the volume of oil in milliliters.

All of the paraffinic material was, therefore, distilled at a pressure of 215 mm Hg. The residues from these distillations were blended and redistilled to obtain a best lot of 3-methylhexane. The result of this final distillation is shown in figure 13.

The boiling points of the distillate from the distillation at 215-mm pressure were determined also at atmospheric pressure as an aid in following the fractionation with respect to the normal boiling points. The scale of the curve of refractive index is enlarged so that small changes in composition may be observed. A change in the refractive index of 0.0025 corresponds to a change of approximately 10 percent between paraffinic and naphthenic content.

A study of the distillation revealed that the lower-boiling paraffin and the naphthenes were preferentially concentrated in the first 40 percent of the distillate. It was pointed out earlier in this section that the difference in boiling points between 215- and 760-mm pressure was about a degree greater for the naphthene than for the paraffin; that is, in distillation at a pressure of 215 mm Hg, the *trans*-1,2-dimethylcyclopentane boils about one degree lower than the 3-methylhexane, whereas the two hydrocarbons have the same boiling point at 1 atmosphere. There was obtained in this way one lot of material that contained over 90 percent of 3-methylhexane.

The concentrate marked "second best" in figure 13 was studied as to possible fractionation in the solid phase. Experiments were made with various solvents, and for one fraction cooled in a mixture of methane and ethane, some crystals were obtained. However, no fractionation was observed when the crystals were separated from the mother liquor. Further attempts to improve this concentrate were discarded, because the purity of the best lot was sufficient to identify this paraffin as 3-methylhexane, which has been prepared in a state of high purity by Edgar and Calingaert [39].

The best lot was treated with silica gel to remove any cracked material (because it was composed of the end fractions in distillation), and the physical constants were determined.

Table 3 gives the properties of the 3-methylhexane from petroleum and those of synthetic 3-methylhexane. Since this petroleum fraction showed no optical activity, the isolated 3-methylhexane must be the *dl* mixture of 3-methylhexane.

This sample exhibited the same behavior on cooling as has been reported for synthetic samples, namely, that on cooling it congeals to a glass [39, 29, 40[6]]. Attempts were made to obtain freezing points by special methods, such as trying to prepare crystals from solvents

[6] It is reported in this literature reference that 3-methylhexane has a freezing point of −119.4° C, as published by Timmermans [42]. However, Timmermans [43] corrected this statement in a later paper by reporting that 3-methylhexane freezes to a glass.

and then seeding with these crystals. In no case, however, was a freezing point realized.

Two determinations of the ratio of the number of moles of H_2O to the number of moles of CO_2 formed in combustion [33] yielded the values 1.1324 and 1.1332. From these data, it was calculated that this material contained 0.070 ±0.005 mole fraction of naphthenic material. Because the possible paraffin hydrocarbons that might be present as impurity boil at least 2° C lower or at least 6° C higher, it is reasonable to assume that this best lot of 3-methylhexane contained no other paraffinic material in significant amount.

TABLE 3.—*Properties of 3-methylhexane*

Properties	3-Methylhexane		
	From petroleum, Glasgow		Edgar and Calingaert
	Actual "best" lot [a]	Extrapolated to a purity of 100 percent [b]	
Boiling point at 760 mm Hg, °C	[c] 91.97 ±0.02	91.96 ±0.07	[d] 91.88
Freezing point in air, °C	(Glass)		(Glass)
Density, g/ml:			
At 20° C	0.6904 ±0.0001	0.6859 ±0.0008	0.6870
At 25° C	.6866 ±0.0001	.6821 ±0.0008	
Refractive index, n_D:			
At 20° C	1.3893 ±0.0001	1.3877 ±0.0005	1.3887
At 25° C	1.3871 ±0.0001	1.3855 ±0.0005	
Critical solution in aniline:			
Temperature, °C	69.1 ±0.2	70.6 ±0.3	70.5
Composition, mole fraction of hydrocarbon	0.58 ±0.02	0.58 ±0.03	
Analytical combustion, moles H_2O/moles CO_2	[e] 1.1328 ±0.0004		

[a] Impurity (presumably *trans*-1,2-dimethylcyclopentane) estimated to be 0.070±0.005 mole fraction.
[b] The purpose of extrapolation to a purity of 100 percent was for comparison with the synthetic 3-methylhexane.
[c] Determined by C. B. Willingham and F. D. Rossini.
[d] Measured with a platinum resistance thermometer by Wojciechowski [44].
[e] Mean and mean deviation of 2 experiments. (See text.)

IX. CONTENT OF 3-METHYLHEXANE, *trans*-1,2-DIMETHYLCYCLOPENTANE, AND *trans*-1,3-DIMETHYLCYCLOPENTANE IN THE PETROLEUM FRACTION

The 6.5-liter fraction distilling between 89.6° and 92.2° C at 760 mm Hg (see figure 2) yielded about 1.6, 1.4, 1.5, and 2.0 liters of 2-methylhexane, *trans*-1,3-dimethylcyclopentane, 3-methylhexane and *trans*-1,2-dimethylcyclopentane, respectively. Referred to the amount of *n*-heptane as unity, the relative amounts of these four hydrocarbons in this petroleum are as follows: 2-methylhexane, 0.28; *trans*-1,3-dimethylcyclopentane, 0.21; 3-methylhexane, 0.25; *trans*-1,2-dimethylcyclopentane, 0.31. A discussion of the accuracy of these estimates is given in reference [41].

X. REFERENCES

[1] J. H. Bruun and M. M. Hicks-Bruun, BS J. Research **10**, 465 (1933) RP542.
[2] J. H. Bruun and M. M. Hicks-Bruun, unpublished work.
[3] M. M. Hicks-Bruun and J. H. Bruun, BS J. Research **8**, 525 (1932) RP432.
[4] J. Pelouze and A. Cahours, Compt rend. **54**, 1241 (1862); **56**, 505 (1863); **57**, 62 (1863).
[5] C. M. Warren, Proc. Am. Acad. Arts Sci. **27**, 56 (1868).
[6] C. Schorlemmer, Ann. Chem. Liebig **136**, 257 (1865).

[7] C. F. Mabery, Proc. Am. Acad. Arts Sci. **31**, 55 (1894).
[8] F. E. Francis and S. Young, J. Chem. Soc. **73**, 921 (1898).
[9] K. W. Charitschkow, Chem. Zentr. **70**, pt. 2, 474 (1899).
[10] N. Costaschescu, Chem. Zentr. **82**, pt. 1, 682 (1911).
[11] J. S. Brame and T. G. Hunter, J. Inst. Petroleum Tech. **13**, 794 (1927).
[12] N. Zelinsky and M. Rudsky, Ber. deut. chem. Ges. **29**, 403 (1896).
[13] W. Markownikoff, Ber. deut. chem. Ges. **30**, 974 (1897); Ann. Chem. Liebig, **301**, 170 (1898).
[14] C. F. Mabery and O. J. Sieplein, Am. Chem. J. **25**, 284 (1901).
[15] L. Balbiano and P. Zeppa, Chem. Zentr. **74**, pt. 2, 1085 (1903).
[16] W. P. White, J. Phys. Chem. **24**, 392 (1920).
[17] J. H. Bruun, R. T. Leslie, and S. T. Schicktanz, BS J. Research **6**, 363 (1931) RP280.
[18] J. H. Bruun and S. T. Schicktanz, BS J. Research **7**, 851 (1931) RP 379.
[19] E. W. Washburn, J. H. Bruun and M. M. Hicks-Bruun, BS J. Research **2**, 467 (1929) RP45.
[20] F. D. Rossini, Proc. Am. Petroleum Inst. **16M**, III, 47 (1935); Oil Gas J. **33**, No. 52, 61 (1935); Refiner Natural Gasoline Mfr. **14**, 255 (1935).
[21] R. T. Leslie, BS J. Research **10**, 609 (1933) RP552.
[22] B. J. Mair and J. D. White, J. Research NBS **15**, 151 (1935); RP817.
[23] S. T. Schicktanz, J. Research NBS **18**, 129 (1937) RP967.
[24] S. T. Schicktanz, unpublished work.
[25] F. W. Rose and J. D. White, J. Research NBS **21**, 167 (1938) RP1123.
[26] J. D. White and A. R. Glasgow, Jr., J. Research NBS **19**, 423 (1937) RP1033.
[27] M. Lecat, Ann. Soc. Sci. Bruxelles **B48**, 107 (1928).
[28] International Critical Tables, **3**, 319 (McGraw-Hill Book Co., New York N. Y. 1928).
[29] J. Smittenberg, H. Hoog, and R. A. Henkes, J. Am. Chem. Soc. **60**, 17 (1938).
[30] G. Chavanne, Bul. soc. chim. Belg. **35**, 283 (1926); Bul. sci. acad. roy. Belg. [12], **5**, 105 (1926).
[31] N. Zelinsky, Ber. deut. chem. Ges. **35**, 2677 (1902).
[32] E. B. Evans, J. Inst. Petroleum Tech. **24**, 321 (1938).
[33] F. D. Rossini, BS J. Research **8**, 121 (1932) RP405.
[34] G. Chavanne, Bul. soc. chim. Belg. **39**, 402 (1930).
[35] G. Chiurdoglu, Bul. soc. chim. Belg. **47**, 363 (1938).
[36] G. S. Parks and H. M. Huffman, Ind. Eng. Chem. **23**, 1138 (1931).
[37] E. W. Washburn, Ind. Eng. Chem. **25**, 891 (1933).
[38] J. D. White and A. R. Glasgow, Jr., J. Research NBS **22**, 137 (1939).
[39] G. Edgar and G. Calingaert, J. Am. Chem. Soc. **51**, 1544 (1929).
[40] G. Egloff, Physical Constants of Hydrocarbons, **1**, 42 (Reinhold Publishing Corporation, New York, N. Y. 1939).
[41] F. D. Rossini, Proc. Am. Petroleum Inst. **18**, III, 36 (1937); Oil and Gas J. **36**, No. 26, 193 (1937); Refiner Natural Gasoline Mfr. **16**, 545 (1937).
[42] J. Timmermans, Bul. soc. chim. Belg. **30**, 62 (1921).
[43] J. Timmermans, Bul. soc. chim. Belg. **36**, 503 (1927).
[44] M. Wojciechowski, Przemysl Chem. **23**, 129 (1939).
[45] F. W. Schwab and Edward Wichers. To be published in the proceedings of the Symposium on "Temperature, its Measurement and Control" held by the American Institute of Physics in November 1939.

WASHINGTON, January 17, 1940.