THE ISOLATION OF THE ISOMERS OF HEXANE FROM PETROLEUM [1]

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ABSTRACT

This paper describes the isolation of four of the five isomers of hexane from an Oklahoma crude petroleum. The fifth isomer, 2-2-dimethylbutane, was not found.

It was found that ordinary fractional distillation concentrated the hexanes in a set of constant-boiling mixtures, the other constituents of which were ring compounds.

These constant-boiling mixtures were broken up by distillation after the addition of an alcohol which was later removed from the distillates by washing with water. In this way, aided by equilibrium melting, the following four hexanes were obtained and identified: 2, 3-dimethylbutane, 2-methylpentane, 3-methylpentane, and n-hexane.

The following constants were determined for each hexane: Boiling point, freezing point, specific gravity, and refractive index.

The freezing points found for two of the hexanes appear to be the only ones on record. They are, for the air-saturated hydrocarbon, $-143 \pm 0.5°$ C. for 2-methylpentane and $-118 \pm 0.5°$ C. for 3-methylpentane. The eutectic for the system CO_2-2-methylpentane is $-153 \pm 0.5°$ C.

CONTENTS

I. INTRODUCTION

A search through the literature reveals the reported isolation of all of the five isomers of hexane from petroleum.[3] The methods employed were usually a combination of distillation and strong chemical treatment, which yielded a mixture of the hexane isomers. By means of chlorination, bromination, or nitration of this mixture the

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corresponding derivatives of the hexanes were obtained, and these derivatives, having larger differences in boiling points, were separated by means of fractional distillation. Some investigators attempted not only to prove in this way the presence of these isomers, but actually to isolate them in pure condition. In this way Sidney Young[4] was able to isolate a small sample of *n*-hexane in fairly pure condition. With this exception, it seems that no one has obtained *n*-hexane or its isomers from petroleum in a demonstrably pure condition.

In recent years other investigators[5] have reported the isolation of the isomers of hexane by using efficient fractionating columns without the aid of chemical reagents. Although the fractions obtained were apparently of higher purity than those previously reported, the evidence as to purity and identity was, however, not complete.

The possibility of isolating pure hydrocarbons from petroleum, by means of fractional distillation alone, seems to depend entirely upon the crude oil used. If this contains cyclic compounds which form constant boiling mixtures with the alipahtic hydrocarbons, a complete separation can not be obtained in this way. If, for instance, methylcyclopentane or benzene is present, constant boiling mixtures with the hexanes will be formed.[6] Since cyclic compounds as a rule have higher densities and higher refractive indices than the aliphatic hydrocarbons, the presence of these ring compounds probably accounts for the fact that these physical constants are always higher for the hexanes reported from petroleum than for the synthetic ones.

II. METHODS EMPLOYED

For the purpose of separating the aliphatic from the cyclic hydrocarbons, it is desirable to avoid any chemical treatment which might destroy certain groups of hydrocarbons or convert them into new compounds from which they could not be readily recovered in their original form. In this investigation, therefore, use has been made only of physical methods.

In order to separate by distillation two liquids of nearly the same boiling point, it is customary to add a third component which alters materially the vapor pressure ratio of the original components; for example, by forming a constant boiling mixture with one of them. A general application of this principle is in practice not always feasible, because difficulties are encountered in removing the added component after distillation. If, however, this component is selected so that it can be extracted by water or some other nonmiscible liquid it offers a very convenient method for separating cyclic from alipathic hydrocarbons.[7]

In separating the ring compounds from the hexanes a liquid, such as absolute ethyl or methyl alcohol, is added in certain proportions and the mixture is subjected to fractional distillation, after which the alcohol is extracted from the distillates with water. Ethyl alcohol forms mixtures of constant minimum boiling point with the isomers of hexane, which all boil below 58.7° C. On the other hand, the con-

[4] J. Chem. Soc., London, **73**, p. 910; 1898.
[5] Anderson and Erskine, Ind. Eng. Chem., **16**, p. 263; 1924; Brown and Carr, Ind. Eng. Chem., **18**, p. 718; 1926.
[6] Young, J. Chem. Soc., London, **73**, Trans., p. 905, 922; 1898.
[7] An industrial application of this method might be used for separating certain groups of (aromatic, cyclic or unsaturated) hydrocarbons of high antiknock value from petroleum fractions.

stant boiling mixtures of ethyl alcohol and ring compounds have boiling points somewhat higher as indicated by the following data, which are taken from the International Critical Tables, Vol. III, page 320.

C_2H_5OH with—	B. P.	Mole per cent of C_2H_5OH
	°C.	
Cyclohexene	66.7	49.5
Cyclohexane	64.9	44.5
Methylcyclohexane	73.0	70.0
Benzene	68.24	44.8
1, 3 Cyclohexadiene	66.7	47.3
n-hexane	58.68	33.2

III. EXPERIMENTAL PROCEDURE

1. FRACTION CONTAINING THE FOUR HIGHER BOILING ISOMERS OF HEXANE

In the present investigation about 30 liters of the naphtha fraction [8] with a boiling range from about $+34°$ to $180°$ C. was subjected to distillation in a current of carbon dioxide in the 20-plate rectifying still described in a previous paper.[9] Fractions from this distillation, having a boiling range of $54°$ to $75°$ C., are represented by the vertical row of rectangles on the left side of the chart shown in Figure 1. This diagram shows the further separation of these fractions.

Each rectangle represents a fraction and the numbers inside the rectangle indicate, respectively, the serial number (at the top) and the refractive index n_D^{20} (at the bottom). Boiling points are not inserted as the distillation was carried out in different stills, in which different thermometers and thermocouples were used, and also because the temperatures recorded were uncorrected and only of laboratory value.

Fractions having similar refractive indices and boiling points were mixed and redistilled in smaller stills of Pyrex laboratory glass with either steel "jack chain" columns or nonsiphoning bubbling-cap plates.[10] Referring to the upper left of the chart shown in Figure 1 (see letter A on chart), fractions Nos. 66^7 and 66^8 were mixed and added to the still pot (indicated by the heavy horizontal line on the top), after which fractions Nos. 116^1, 116^2, 116^3, 116^4, 116^5, 116^6, and 116^7 were distilled off. In many cases the fractions were added to the still pot at intervals during the distillation. For instance, at the lower right of Figure 1 (see letter B on chart) fractions Nos. 126^7, 126^8, and 126^9 were initially mixed in the still pot. Fraction 126^{19} was then distilled off after which 126^{10} was added to the still pot, 126^{20} was next distilled off, etc.

The unbroken lines in the chart indicate that the distillation was carried out without the previous addition of a third component, the dotted lines indicate that methyl alcohol was added to the still pot, while the dashed lines show that ethyl alcohol was used as a third

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[8] The crude was obtained from No. 6 well of the South Ponca Field, Kay County, Okla. See B. S. Jour. Research, **2**, p. 469, Table 1; 1929.
[9] Washburn, Bruun, and Hicks, B. S. Jour. Research, **2**, pp. 470–473; 1929.
[10] J. H. Bruun, Ind. Eng. Chem., Anal. ed., **1**, p. 212; 1929.

component. For instance, referring to the center of the chart (fig. 1) (see letter C on chart), fractions 117^5, 117^6, 114^4, 114^5, and 114^6 were mixed with methyl alcohol and added to the still pot. Fractions 117^{12}, 117^{13}, and 117^{14} were then distilled off after which fractions 117^7, 117^8, 114^7, 114^8, and 115^4 and more methyl were added to the still pot. Fractions 117^{15}, 117^{16}, 117^{17}, 117^{18}, and 117^{19} were then distilled off, etc. With this explanation, the chart is self-explanatory.

Freezing point curves were made for fractions 64^5, 64^6, 64^7, 64^8, 64^9, and 65^1, which had refractive indices ranging from 1.387 to 1.407. The freezing ranges were from $-95°$ to $-60°$ C. This suggested that effective fractionation could be obtained by equilibrium melting [11] (indicated by "D"). Therefore, each fraction was frozen, melted slowly, and separations made according to the melting points. In each case the fractions so obtained were classified into the groups shown in Table 1.

TABLE 1

Group	M. P. range	Refractive index $n\frac{20}{D}$
I	$-95°$ to $-115°$ C	1.389 to 1.406.
II	$-70°$ to $-95°$ C	1.382 to 1.389.
III	$-30°$ to $+5°$ C	1.392 to 1.413.

Group II, which was the largest group, contained the hexanes, as indicated by the melting point range, index of refraction, and boiling point range. Fractionation of these three groups was continued, in some cases alternating the equilibrium melting with distillation. The ranges of the indices of refraction of the fractions contained in Groups I and III in Table 1 are very similar, while their freezing points differ by more than 100° C. By further equilibrium melting the groups shown in Table 2 were obtained.

TABLE 2

Group	M. P. range	B. P. range	Refractive index $n\frac{20}{D}$
I	$-100°$ to $-115°$ C	70° to 73° C	1.397 to 1.410.
II	$-93°$ to $-95°$ C	69° to 69.5° C	1.378 to 1.384.
III	$-30°$ to $+5°$ C	77.5° to 81° C	1.407 to 1.453.

The section of Group II in Table 2 containing compounds having refractive indices from 1.380 to 1.383 was then mixed with fractions from serial Nos. 91 to 92. (See fig. 1.)

Concerning Group III in Table 2 it may be noted that although no serious attempt was made to isolate the pure constituents, the odor resembled that of benzene. Also the freezing point (around $+5$), the boiling point (about 81) and the refractive index (1.453) after several crystallizations approached more and more the values of pure benzene. The presence of a constant boiling mixture (boiling point around 69° C.) of benzene with the hexane would also explain why only small amounts of benzene would be obtained at the proper boiling point (79.6° C.) during a straight distillation of the crude oil.

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[11] M. M. Hicks, B. S. Jour. Research, 2, pp. 483–486; 1929.

Group I in Table 2 will, perhaps, be found to consist mainly of methylcyclopentane which has the following physical constants: Boiling point, 73° C.;[12] melting point, − 140.5° C.;[12] and refractive index $n\frac{20}{D}$, 1.410.[13]

As we approach the lower end of the diagram the refractive indices of the hexane fractions are decreasing, which indicates the separation of the cyclic and aromatic compounds. Compounds with high refractive indices were concentrated in the fractions on the right hand of the diagram and were gradually eliminated.

As a result of this procedure all the possible isomers of hexane were obtained with the exception of 2,2-dimethylbutane, the boiling point (49.7° C.) of which lies outside the range of this material. The search for this low boiling isomer is described below (p. 938).

The physical constants determined for the final fractions, together with some of the most reliable values recorded in the literature for the corresponding synthetic compounds, are given in Table 3. The data on refractive indices and specific gravities given by other investigators have been rounded off.

TABLE 3.—*Physical constants of the isolated hydrocarbons*

Compound	Boiling point corrected 760 mm	Freezing point °C. (in air)	Refractive index 20 n_D	Specific gravity 20°/4°C.
2, 3-dimethylbutane:				
(Series No. 114 [3]=40 ml)[a]	58.0	−135±1	1.378	0.668
(Series No. 126 [21]=40 ml)	58.3	----------	1.376	.665
Synthetic:				
Data compiled by Edgar and Calingaert [b]	[c] 58.1	----------	[d][e] 1.377	[c] .662
Beilstein Erg. Bd. 1, p. 55; 1928	[f] 58.7	[g] −135	----------	----------
2-methylpentane:				
(Series No. 119[3]=100 ml)	60.4	−143±0.5	1.374	.659
(Series No. 126[23]=120 ml)	60.6	----------	1.373	.658
Synthetic:				
Data compiled by Edgar and Calingaert [b]	[c] 60.2	----------	[d][e] 1.371	[e] .654
Beilstein Erg. Bd. 1, p. 53; 1928	----------	----------	1.374	----------
3-methylpentane:				
(Series No. 110 [3]=60 ml)	63.3	−118±0.5	1.376	.665
(Series No. 127 [3]=50 ml)	63.2	----------	1.375	.662
Synthetic:				
Data compiled by Edgar and Calingaert [b]	[c] 63.2	----------	[d][e] 1.376	[e] .665
Beilstein Erg. Bd. 1, p. 54; 1928	63.5 to 65.5	----------	1.377	.667296
n-hexane (Ser. No. 126 [35])[h]	68.84	−97.2±0.5	1.379	.673
Synthetic:				
Timmermans [i]	68.80	−95.0	1.375	.659
Beilstein Erg. Bd. 1, p. 51; 1928 and Vol. I, p. 143; 1918	[j] 68.95	[k] −94.3	[l] 1.375	[d] .660
According to Mair [m]	68.68	−95.4±0.1	1.375	----------

[a] The molecular weight was found to be 85.7±0.5; theoretical=86.10. For method see B. S. Jour. Research, **5**, p. 575; 1930.
[b] J. Am. Chem. Soc., **51**, p. 1546; 1929.
[c] Chavanne, Bull. Soc. Chim. Belg., **31**, p. 331; 1922.
[d] Lowry, J. Chem. Soc., **105**, p. 91; 1914.
[e] Chavanne and Van Risseghem, Bull. Soc. Chim. Belg., **31**, p. 87; 1922.
[f] At 762 mm. pressure.
[g] From Int. Crit. Tables, **1**, p. 204.
[h] The molecular weight was found to be 85.6±0.3; theoretical=86.10.
[i] Timmermans, J. Chim. Phys., **25**, p. 411; (1928).
[j] Young, J. Chem. Soc., **73**, p. 906; 1898.
[k] Timmermans Chem. Zentr., **II**, p. 1015; 1911.
[l] Brühl Lieb. Ann., **200**, p. 184; 1880.
[m] Bureau of Standards, unpublished.

[12] From Int. Crit. Tables, **I**, p. 202.
[13] Kijner, J. Prakt. Chem., **56**, p. 364; 1897.

2. A SEARCH FOR 2, 2-DIMETHYLBUTANE

The physical constants of synthetic $(CH_3)_3C-CH_2CH_3$ are: [14]

Boiling point	49. 7°C.
Refractive index $n\frac{20}{D}$	1. 369
Specific gravity $\frac{20}{4}$	. 649
Melting point	−98. 2°C.

Six hundred gallons of crude oil [15] was distilled in a semicommercial still in an oil refinery.[16] The lower boiling fractions from this distillation were fractionated in a 20-plate laboratory bubbling-cap still.[17] The fractions from the laboratory still having boiling point ranges from 40° to 55°C. were subjected to distillation in smaller Pyrex laboratory glass stills.[18] Between 40° and 52°C., 1,700 ml was obtained and after two more distillations in the glass stills fractions with the boiling points and refractive indices shown in Table 4 were obtained.

TABLE 4.—*Properties of the final fractions obtained in a search for 2, 2-dimethylbutane*

Boiling range (°C.)	Volume	Refractive index at 20° C.
	ml	
36–38	100	
38–40	120	
40–42	240	1. 367
42–44	270	1. 372
44–46	135	1. 377
46–47	110	1. 376
47–48	140	1. 381
48–49	120	1. 379
49–50	74	1. 384
50–51	30	1. 390
51–57	150	1. 381
Total	1, 489	

Careful fractionation of the 1,700 ml of the combined fractions with boiling point range 46° to 52° C. did not yield more than a very small amount of liquid at the boiling point of 2, 2-dimethylbutane. The comparatively high refractive indices of these higher boiling fractions indicate that they may be mixtures of cyclic hydrocarbons and the two isomers of hexane (boiling points 58° and 60° C.), the presence of which has been shown on page 937.

Because of the fact that the fractions from our laboratory stills (equipped with condensers cooled with solid CO_2) contained several liters of constituents boiling below 50° C., it seems reasonably safe to assume that the 2, 2-dimethylbutane was not lost by evaporation before or during the industrial distillation in which ice water was employed on the condenser. The very small amount (74 ml) of distillate which was obtained between 49° and 50° C. as well as the

[14] International Critical Tables, **1**, p. 204.
[15] From the well mentioned in footnote 8, p. 935.
[16] Acknowledgment for this distillation is made to A. E. Pew, jr., and R. B. Davidson, of the Sun Oil Co.
[17] See footnote 8, p. 935.
[18] See footnote 10, p. 935

FIGURE 1.—Ancestral chart of the hexanes

Legend:
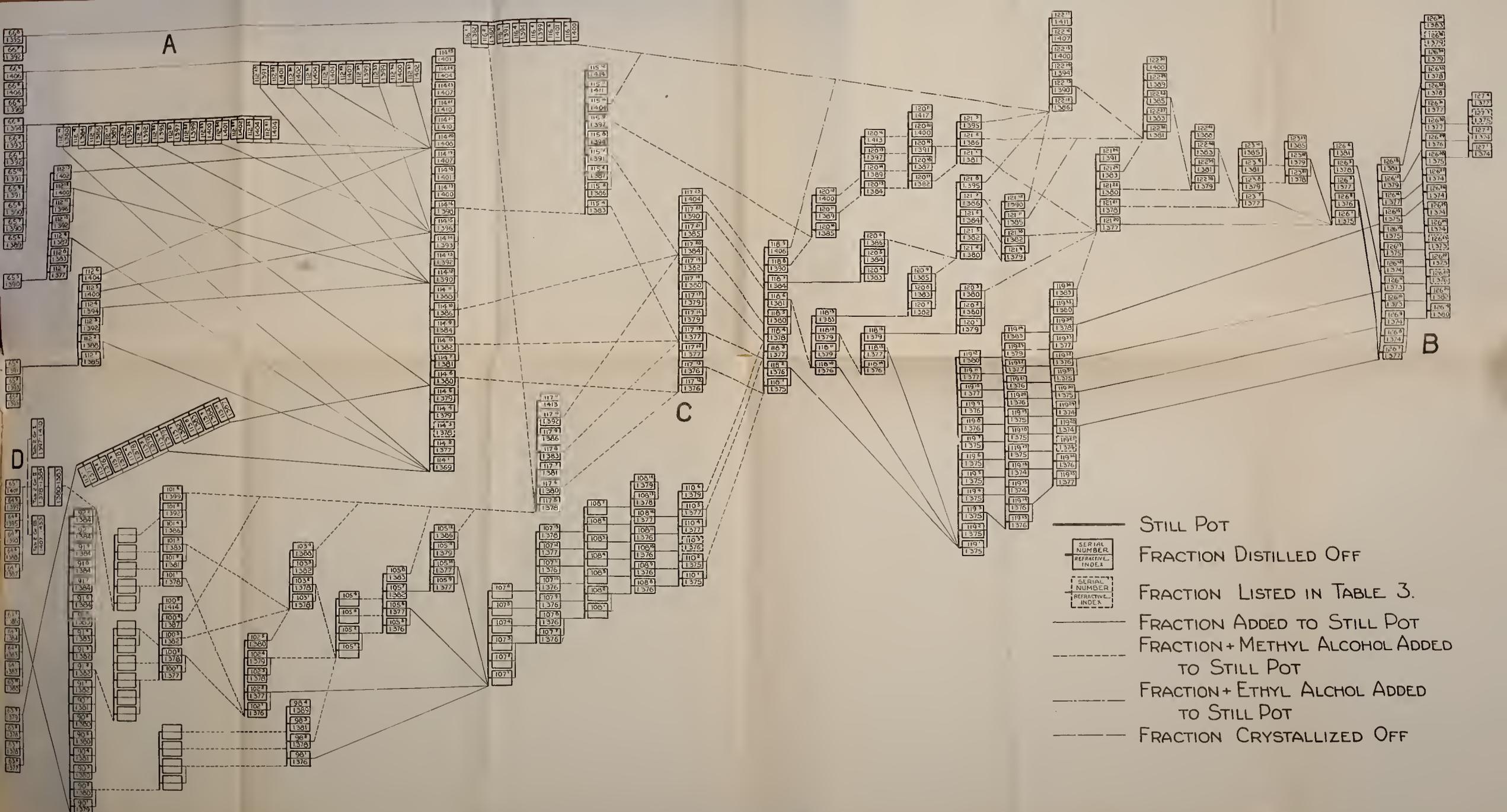
Symbol	Meaning
————	STILL POT
(solid box) SERIAL NUMBER / REFRACTIVE INDEX	FRACTION DISTILLED OFF
(dashed box) SERIAL NUMBER / REFRACTIVE INDEX	FRACTION LISTED IN TABLE 3.
——————	FRACTION ADDED TO STILL POT
– – – – –	FRACTION + METHYL ALCOHOL ADDED TO STILL POT
· · · · ·	FRACTION + ETHYL ALCOHOL ADDED TO STILL POT
– · – · –	FRACTION CRYSTALLIZED OFF

comparatively high refractive index (1.384 against 1.369 for 2, 2-dimethylbutane) of the distillate would indicate that the 2, 2-dimethylbutane is absent or if present the percentage must be less than 0.01 of the crude. It should be noted, however, that the possibility of the presence of 2, 2-dimethylbutane in the crude oil is not completely excluded unless the absence of constant boiling mixtures of this hexane with other constituents is proved.

IV. DISCUSSION OF RESULTS

1. THE 2, 3-DIMETHYLBUTANE FRACTION

The values of the five properties recorded in Table 3 for this fraction show excellent agreement with those of the synthetic hydro-
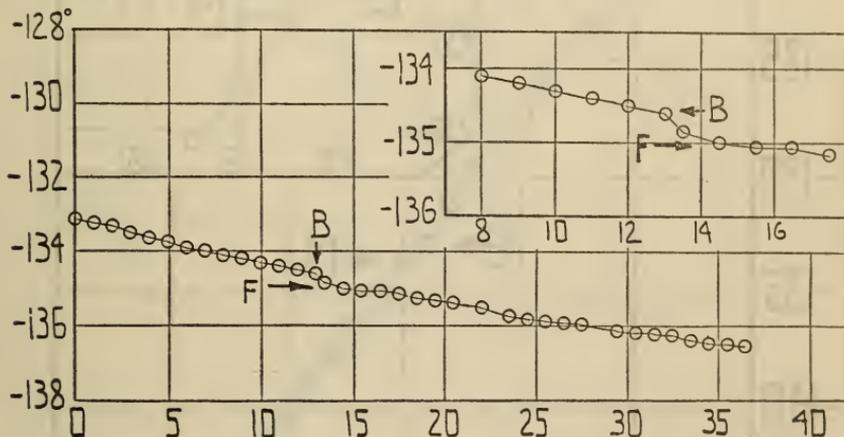
FIGURE 2.—*Cooling curve for 2, 3-dimethylbutane, C_6H_{14}*

Ordinates, temperature in ° C.   Abscissas, time in minutes.

carbon. The agreement with respect to the freezing point is the most significant, however, since the other four properties alone are not very distinctive for the hexane isomers. The cooling and heating curves for this fraction are shown in Figures 2 and 3. At the point B in Figure 2 crystallization begins. From B to F the temperature falls, owing to the increasing concentration of the dissolved air in the liquid phase. At F the liquid has become saturated with dissolved air, and the system becomes nonvariant as evidenced by the three to four minute halting point at $-135°$ C., which is the freezing point of the air-saturated hydrocarbon. On the heating curve (fig. 3) liquefaction does not begin until about $-134°$. The latent heat of fusion is evidently very small.

2. THE 2-METHYLPENTANE FRACTION

Here only three properties are available for comparison. The agreement is satisfactory, but is not sufficient evidence of identity unless it can be demonstrated that the fraction is not a mixture. In order to obtain evidence on this point, the cooling curve was determined with the results shown in Figure 4. These results are

satisfactory as far as they go, but it was noticed that the liquid became very viscous at its freezing point, so viscous in fact that the stirrer ceased to operate, and crystallization may, therefore, not have been complete.

In order to avoid this difficulty the hydrocarbon was cooled to about $-50°$ and then saturated with solid CO_2. The dissolved CO_2
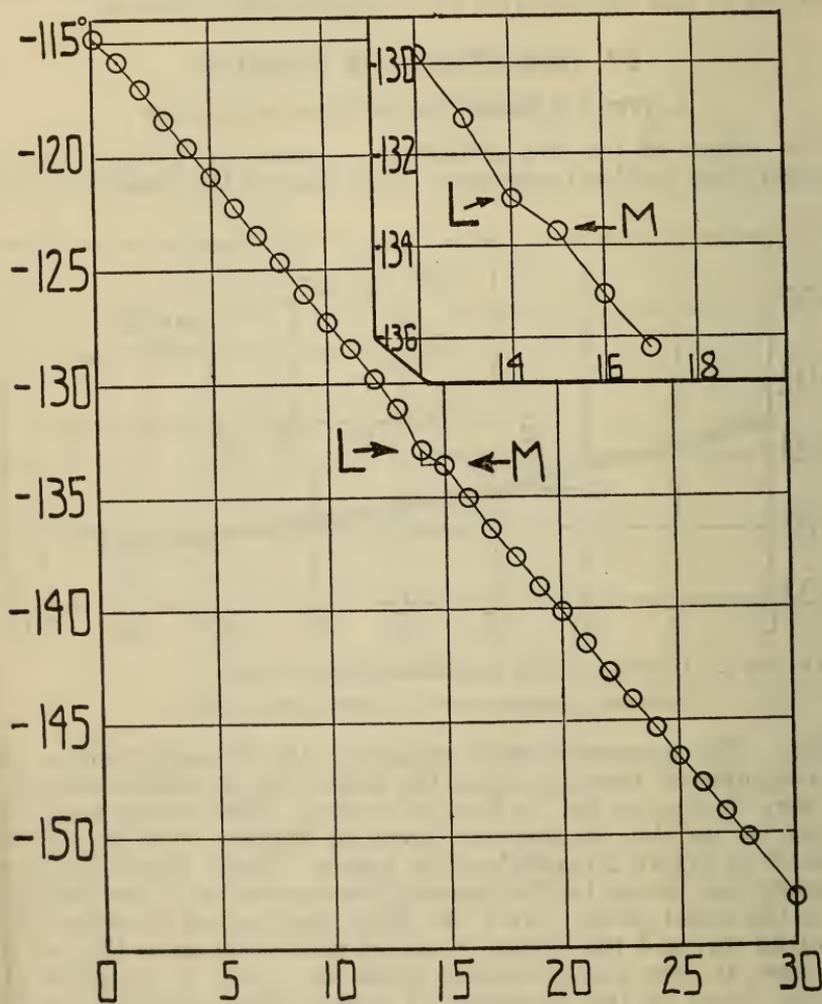
FIGURE 3.—*Heating curve for 2, 3-dimethylbutane, C_6H_{14}*

Ordinates, temperature in ° C.   Abscissas, time in minutes

materially increased the fluidity. The cooling curve was then determined through the eutectic, with the results shown in Figure 5. The thermocouple was placed in the center of the sample, and freezing started on the walls of the container and proceeded toward the center. The long halting point followed by the sharp drop in temperature at the completion of crystallization is evidence of purity.[19]

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[19] The shorter halting point in the second experiment is due to the use of a heavier walled containing vessel and a consequent increase in the heat capacity of the system.
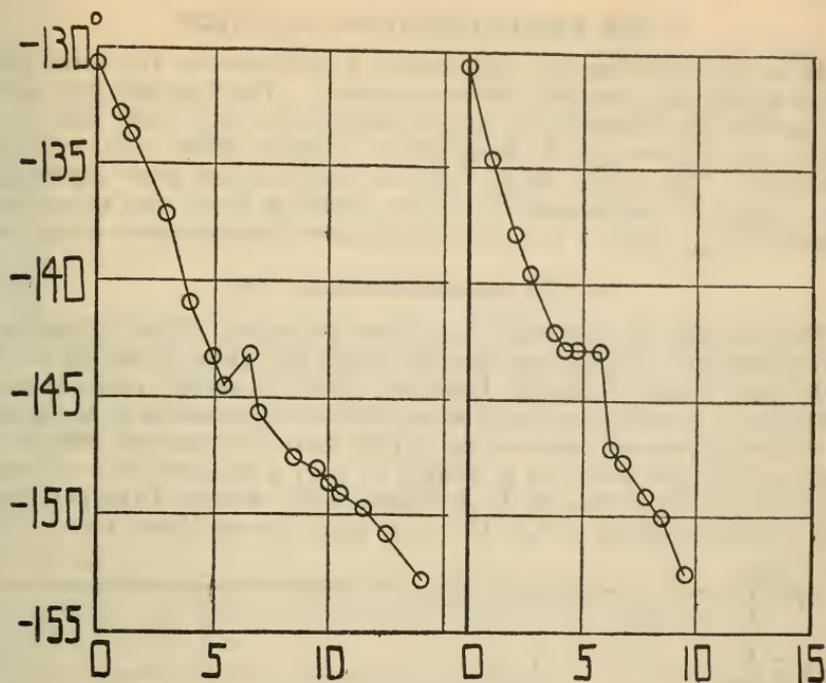
FIGURE 4.—*Two cooling curves for 2-methylpentane, C_6H_{14}*

Ordinates, temperature in ° C.   Abscissas, time in minutes.
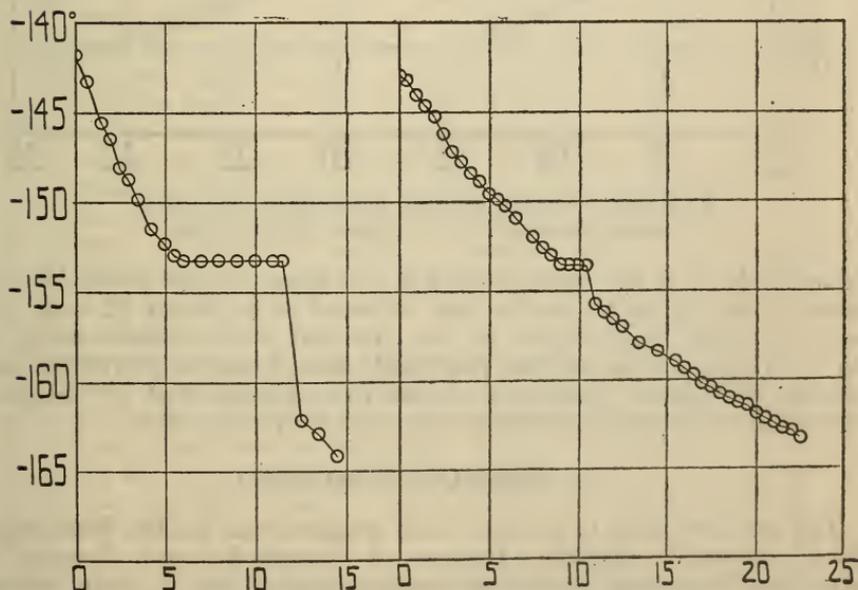
FIGURE 5.—*Cooling curve for carbon dioxide eutectic with 2-methylpentane,*
C_6H_{14}

Ordinates, temperature in ° C.   Abscissas, time in minutes.

3. THE 3-METHYLPENTANE FRACTION

As in the preceding case, agreement is excellent for the three properties which are available for comparison. The fraction was tested for purity by determining its freezing behavior, with the result shown in Figure 6. A satisfactory halting point was evidently obtained. The initial small drop in temperature after crystallization begins is the normal behavior resulting from the presence of dissolved air, which is very soluble in these hydrocarbons when cold.

4. THE N-HEXANE FRACTION

This fraction is obviously not pure *n*-hexane. The approximate agreement as to properties, together with the value obtained for the molecular weight indicate, however, that its major constituent is *n*-hexane. In order to obtain quantitative information as to amount of *n*-hexane present two cooling curves were determined, one on the fraction and the other on a sample of very pure synthetic *n*-hexane prepared in this bureau by B. J. Mair. The *n*-hexane from petroleum had a freezing point of 1.8° C. lower than the synthetic one. From
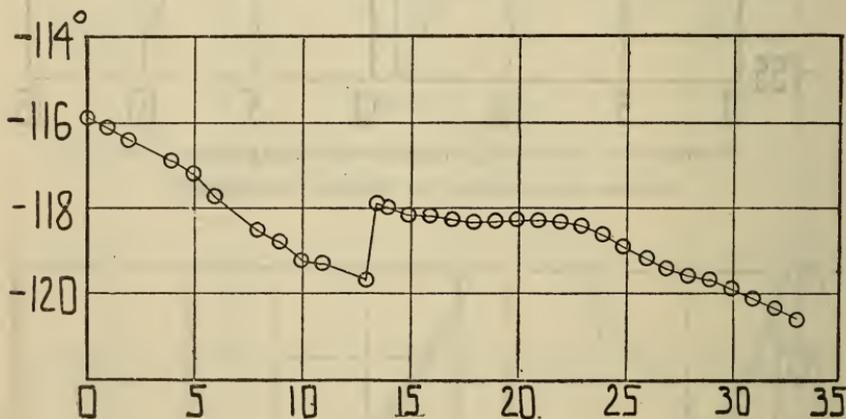
FIGURE 6.—*Cooling curve for 3-methylpentane,* C_6H_{14}
Ordinates, temperature in ° C. Abscissas, time in minutes.

these results and the value 34.89 cal. per gram for the molal heat of fusion,[20] the purity of the fraction is found to be about 92 mole per cent. Further purification of the fraction seems unnecessary at present because *n*-hexane has previously been found in petroleum and because additional quantities of this hydrocarbon will be obtained from other petroleum fractions now under investigation.

V. ACKNOWLEDGMENT

The authors wish to express their gratitude to E. W. Washburn, chief, chemistry division, Bureau of Standards, and director of American Petroleum Institute research project No. 6, under whose direction this investigation has been conducted. We are indebted to J. F. Fox for drawing the chart in Figure 1.

WASHINGTON, April 1, 1930.

[20] Parks and Todd, J. Ind. Eng. Chem., **21**, p. 1236; 1929.