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## ISOLATION OF 1,2,3,4-TETRAMETHYLBENZENE, 5,6,7,8-TETRAHYDRONAPHTHALENE, 1-METHYL-5,6,7,8-TETRAHYDRONAPHTHALENE, AND 2-METHYL-5,6,7,8-TETRAHYDRONAPHTHALENE FROM PETROLEUM<sup>1 2</sup>

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### ABSTRACT

This paper reports the isolation of four additional aromatic hydrocarbons from the kerosene fraction of the petroleum being investigated by the American Petroleum Institute Research Project 6. Their separation was accomplished by a combination of the physical methods of fractionation of azeotropic distillation and crystallization. "Best" lots of each of these four hydrocarbons from petroleum were prepared, and synthetic lots of three of them were purified for purposes of identification and determination of properties. The amounts of impurity in these various lots of material were determined as follows, in mole fraction:

Hydrocarbon	From petroleum	From synthetic material
1,2,3,4-Tetramethylbenzene.....	0. 0006 ± 0. 0001	
5,6,7,8-Tetrahydronaphthalene ---	. 015 ± . 002	0. 0057 ± 0. 0008
1-Methyl-5,6,7,8-tetrahydro- naphthalene.....	. 0029 ± . 0004	. 0034 ± . 0005
2-Methyl-5,6,7,8-tetrahydro- naphthalene.....	. 0046 ± . 0007	. 031 ± . 004

Values of certain physical properties of these four hydrocarbons, all extrapolated to zero impurity, were determined as follows:

<sup>1</sup> Presented before the Division of Petroleum Chemistry at the meeting of the American Chemical Society at Atlantic City, N. J., September 8 to 12, 1941.

<sup>2</sup> 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.

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Property	1,2,3,4-Tetramethylbenzene	5,6,7,8-Tetrahydronaphthalene
Boiling point at 760 mm, °C.....	205.04 ±0.03	207.57 ±0.10
Freezing point in air at 1 atm, °C.....	-6.25 ±0.01	-35.80 ±0.02
Density at 25° C, g/ml.....	0.9015 ±0.0001	0.9662 ±0.0002
Refractive index at 25° C:		
$n_c$ .....	1.51362 ±0.00007	1.53466 ±0.00015
$n_D$ .....	1.51811 ±0.00007	1.53919 ±0.00015
$n_F$ .....	1.52923 ±0.00007	1.55065 ±0.00015
Specific dispersion at 25° C ( $n_F - n_c$ )/ $d$ .....	0.01732 ±0.00005	0.01655 ±0.00010

Property	1-Methyl-5,6,7,8-tetrahydronaphthalene	2-Methyl-5,6,7,8-tetrahydronaphthalene
Boiling point at 760 mm, °C.....	234.35 ±0.05	229.03 ±0.05
Freezing point in air at 1 atm, °C.....	-22.90 ±0.03	-39.75 ±0.03
Density at 25° C, g/ml.....	0.9682 ±0.0002	0.9500 ±0.0002
Refractive index at 25° C:		
$n_c$ .....	1.53738 ±0.00010	1.52920 ±0.00010
$n_D$ .....	1.54190 ±0.00010	1.53365 ±0.00010
$n_F$ .....	1.55325 ±0.00010	1.54498 ±0.00010
Specific dispersion at 25° C ( $n_F - n_c$ )/ $d$ .....	0.01639 ±0.00005	0.01662 ±0.00005

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## I. INTRODUCTION

This paper constitutes the second report of the work on hydrocarbons in the kerosene fraction of petroleum begun carried on at this Bureau as part of the work of the American Petroleum Institute Research Project 6. There are described the isolation and identification of 1,2,3,4-tetramethylbenzene, 5,6,7,8-tetrahydronaphthalene, 1-methyl-5,6,7,8-tetrahydronaphthalene, and 2-methyl-5,6,7,8-tetrahydronaphthalene.

## II. OUTLINE OF THE INVESTIGATION

The diagram in figure 1 shows schematically the last few steps in the work previously reported [1]<sup>4</sup> and the steps in the work covered by this report. There has been given in detail in the first report [1] the method of obtaining the aromatic fractions shown in the block at the head of figure 1, by extraction and adsorption from a series of narrow-boiling kerosene fractions which distilled between 114° and 144° C at 56 mm Hg (approximately 200° to 230° C at 760 mm Hg), together with a description of the distillation at 56 mm of these aromatic fractions and the isolation of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene by crystallization. The work covered by the present report begins with a distillation at 56.8 mm Hg and the production of the second series of constant-boiling fractions shown in figure 1. Then by azeotropic distillation and fractional crystallization, 1,2,3,4-tetramethylbenzene and 5,6,7,8-tetrahydronaphthalene were isolated from the fractions which distilled between 118° and 120.5° C at 56.8 mm Hg; 2-methyl-5,6,7,8-tetrahydronaphthalene from the fractions which distilled between 137° and 140° C at 56.8 mm Hg; and 1-methyl-5,6,7,8-tetrahydronaphthalene from the fractions which distilled between 141° and 144° C at 56.8 mm Hg. As shown in figure 1, additional quantities of the 1- and 2-methylnaphthalenes were also isolated. The former was concentrated in a nearly pure condition by distillation alone in the fractions which distilled from 150° to 151° C at 56.8 mm Hg, while the latter was obtained by azeotropic distillation from the fractions distilling between 144° and 148° C at 56.8 mm Hg. The material distilling in the region from 148° to 150° C at 56.8 mm Hg consisted substantially of a mixture of 1- and 2-methylnaphthalenes.

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

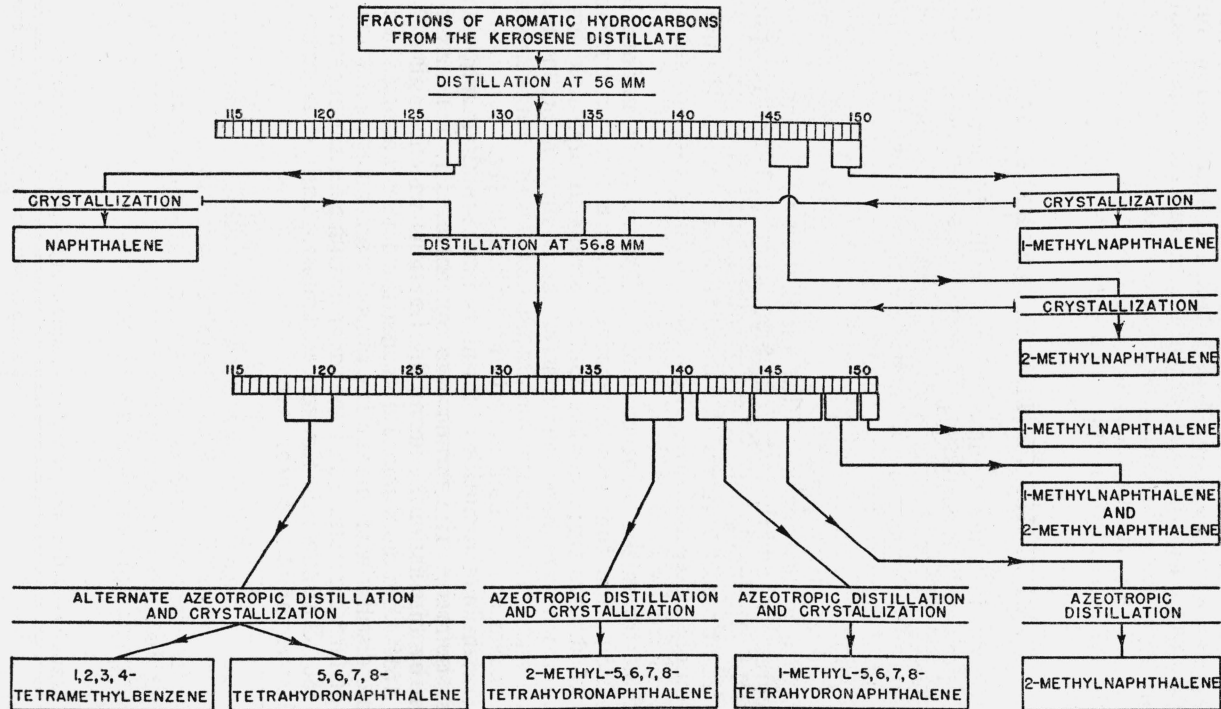


FIGURE 1.—Schematic outline of the investigation.



### III. SYSTEMATIC DISTILLATION AND SOME PROPERTIES OF THE DISTILLATION FRACTIONS

As stated in the preceding paragraph, the work covered by this report began with the systematic distillation at 56.8 mm Hg and the production of the second series of distillate fractions shown in figure 1. This distillation was performed in a column which had a rectifying section 2.5 by 280 cm and a separating efficiency corresponding to about 100 theoretical plates [2]. The reflux ratio was about 40 to 1, and the distillate was removed at a rate of about 9 ml per hour and collected in fractions of 50 ml.

Figure 2 gives the distribution by volume of the distillate with respect to the boiling point at 56.8 mm, and also shows the corresponding variation of the refractive indices of the distillate fractions. The large volume and high refractive indices in the region 118° to 120.5° C, from which 1,2,3,4-tetramethylbenzene (prehnitene) and 5,6,7,8-tetrahydronaphthalene (tetralin) were isolated, may be observed. Similarly, the large volumes and high refractive indices from 137° to 140° C, and from 141° to 144° C, correspond to the regions from which 2-methyl-5,6,7,8-tetrahydronaphthalene and 1-methyl-5,6,7,8-tetrahydronaphthalene, respectively, were isolated. The very high refractive indices of the fractions distilling above 145° C show the presence of considerable quantities of the 2- and 1-methylnaphthalenes.

### IV. SEPARATION OF THE INDIVIDUAL HYDROCARBONS

The first step in the isolation of the individual hydrocarbons from the distillation fractions was the separation by azeotropic distillation (in one case by azeotropic distillation and fractional crystallization) of fractions which were very concentrated in the desired hydrocarbons. The pure hydrocarbons were then isolated from these concentrates by crystallization, as described in section V of this paper.

Since a detailed description of the procedures used in this laboratory for the separation of hydrocarbons by azeotropic distillation has recently been published [3], only a brief description will be given here. All the azeotropic distillations discussed here were performed at 217 mm Hg pressure with diethylene glycol monomethyl ether as the azeotrope-forming substance, in columns having a separating efficiency equivalent to about 100 theoretical plates. The reflux ratio was approximately 45 to 1 and the rate of removal of distillate about 15 ml per hour. Except in the case of 2-methylnaphthalene, sufficient azeotrope-forming substance was used so that all the hydrocarbon was obtained in the distillate. The oil was recovered from the azeotropic distillate fractions by washing with water. The boiling ranges of the azeotropic distillate fractions and their composition are given in table 1. The boiling point of diethylene glycol monomethyl ether at 217 mm Hg is 152.8° C.

TABLE 1.—Boiling ranges and compositions of the azeotropic distillate

	Aromatic fractions distilling at 56.8 mm over the ranges—			
	118° to 120.5° C	137° to 140° C	141° to 144° C	144° to 148° C
Boiling range of the azeotropic distillate at 217 mm, °C.....	141 to 147.5	144 to 151.7	145 to 151.7	147 to 152.8
Volume of oil in the azeotropic distillate, percent. ....	55 to 50	30 to 20	25 to 15	18 to <1

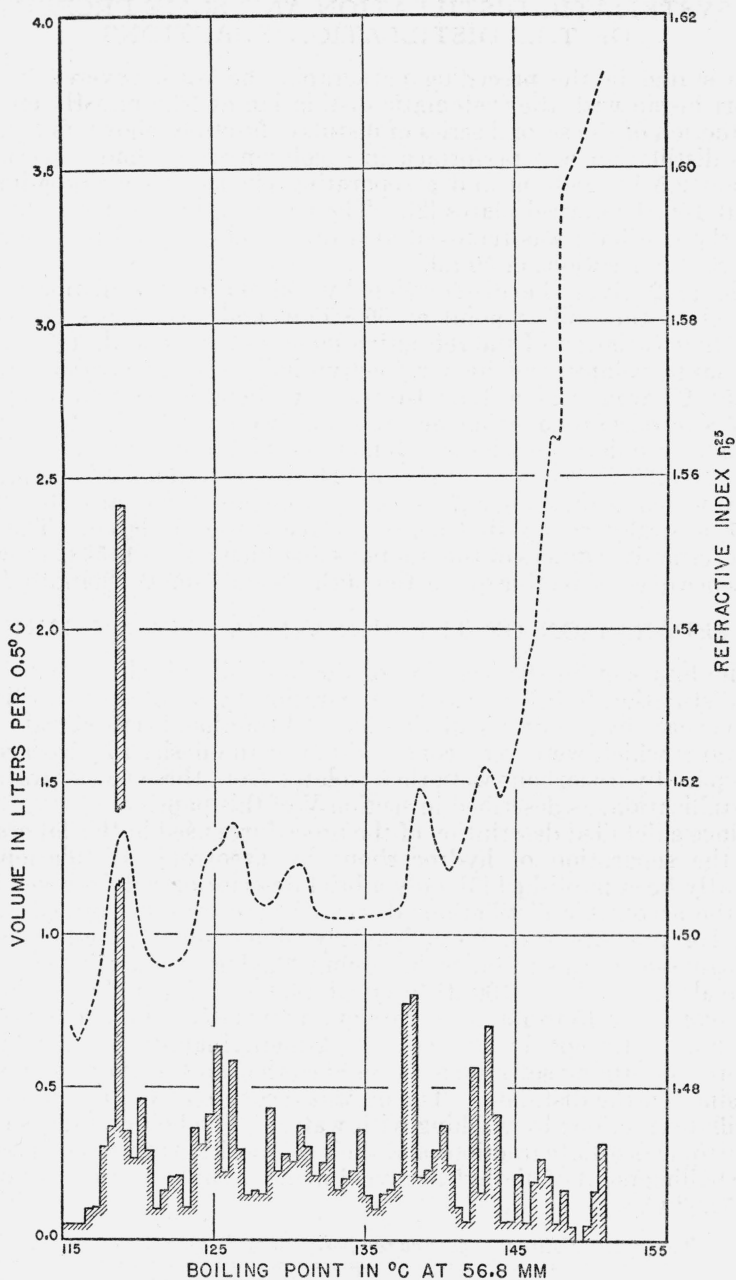


FIGURE 2.—Refractive indices and volume of the distillation fractions plotted with respect to the boiling range.

1. SEPARATION OF 1,2,3,4-TETRAMETHYLBENZENE AND  
5,6,7,8-TETRAHYDRONAPHTHALENE

The separation resulting from the azeotropic distillation of a typical charge of material from the region  $118^{\circ}$  to  $120.5^{\circ}$  C at 56.8 mm Hg is shown in part 1 of figure 3, in which the refractive indices ( $n_D^{25}$ ) of the oil fractions obtained from the azeotropic distillate are plotted with respect to the percentage of the hydrocarbon recovered from the distillate. The wide spread in the refractive indices of the fractions from this distillation is evident. The fractions with refractive indices between 1.51 and 1.52 crystallized readily (those with refractive indices around 1.518 as high as  $-22^{\circ}$  C), and on fractionation by crystallization yielded 1,2,3,4-tetramethylbenzene. The fractions with indices of 1.534 or higher crystallized at about  $-40^{\circ}$  C, and yielded 5,6,7,8-tetrahydronaphthalene on crystallization. Thus the charge was separated by azeotropic distillation into portions rich in 5,6,7,8-tetrahydronaphthalene and 1,2,3,4-tetramethylbenzene, respectively, and a portion rich in a mixture of the mono-, di-, or trialkylbenzenes. The separation of 1,2,3,4-tetramethylbenzene and 5,6,7,8-tetrahydronaphthalene from all the fractions distilling in the region from  $118^{\circ}$  to  $120.5^{\circ}$  C at 56.8 mm Hg was accomplished by azeotropic distillation, followed by the separation of 1,2,3,4-tetramethylbenzene from the fractions with indices between 1.51 and 1.52 by crystallization from dichlorodifluoromethane and centrifuging.<sup>5 6</sup>

The fractions with refractive indices ( $n_D^{25}$ ) above 1.534 were reserved as 5,6,7,8-tetrahydronaphthalene concentrates, and the fractions with indices below 1.50 were considered to be substantially free from 1,2,3,4-tetramethylbenzene and to consist principally of mono-, di-, or trialkylbenzenes. All the other fractions, and the mother liquors from the crystallization of 1,2,3,4-tetramethylbenzene, were blended according to their refractive indices, redistilled azeotropically, and their resolution, by alternate crystallization and azeotropic distillation, into 1,2,3,4-tetramethylbenzene, 5,6,7,8-tetrahydronaphthalene, and material of low refractive index was continued as far as was practical.

## 2. SEPARATION OF 2-METHYL-5,6,7,8-TETRAHYDRONAPHTHALENE

The separation resulting from the azeotropic distillation of a typical charge of material from the region  $137^{\circ}$  to  $140^{\circ}$  C at 56.8 mm Hg (see fig. 2) is shown in part 2 of figure 3. The close approach of the values for the refractive indices of the distillate fractions from the last third of the distillation to the value for the refractive index of 2-methyl-5,6,7,8-tetrahydronaphthalene is apparent. The fractions with refractive indices ( $n_D^{25}$ ) above 1.529 crystallized at about  $-50^{\circ}$  C and were segregated as 2-methyl-5,6,7,8-tetrahydronaphthalene concen-

<sup>5</sup> The centrifuge used in this work was constructed by the International Centrifuge Co. of Boston, Mass. It was similar to one of their standard centrifuges (catalog No. 418), except that the draining chamber was provided with a double jacket to contain the refrigerant and was insulated. The metal basket was 5 inches in diameter and the maximum speed of rotation was 3,600 rpm. The crystals were retained on a 200-mesh wire cloth which was fitted within the basket. This centrifuge gave crystals exceptionally free from mother liquors and was satisfactory for operations down to about  $-80^{\circ}$  C. In this investigation all the crystallizations were performed with the aid of this centrifuge.

<sup>6</sup> In preliminary experiments it was found that some of the fractions from the peak in volume distilling between  $118^{\circ}$  and  $119^{\circ}$  C (particularly those distilling from  $118.7^{\circ}$  to  $118.9^{\circ}$  C) at 56.8 mm Hg yielded crystals on cooling to about  $-55^{\circ}$  C. Some 1,2,3,4-tetramethylbenzene was separated from these fractions by fractional crystallization. An attempt to concentrate the 1,2,3,4-tetramethylbenzene in the mother liquor by distillation to a point where crystallization could again be effectively employed proved unsuccessful.

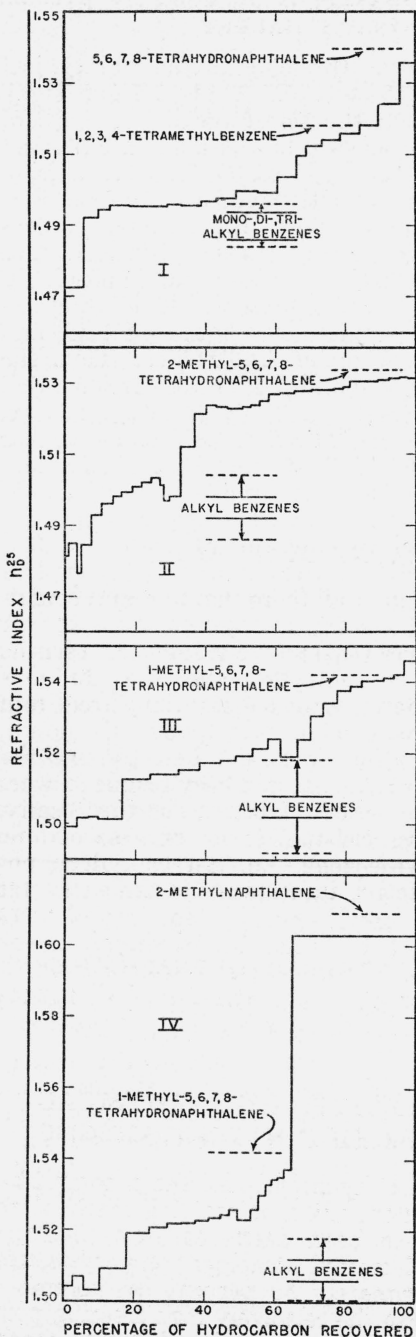


FIGURE 3.—Diagrams illustrating the separation of various hydrocarbons by azeotropic distillation.

trates, while the fractions with refractive indices below 1.505 were considered to consist substantially of alkylbenzenes. The intermediate fractions were blended on the basis of their refractive indices and were separated, as far as was practical, into the aforementioned portions by repeated azeotropic distillations.

### 3. SEPARATION OF 1-METHYL-5,6,7,8-TETRAHYDRONAPHTHALENE

The separation resulting from the azeotropic distillation of a typical charge of material from the region  $141^{\circ}$  to  $144^{\circ}$  C at 56.8 mm Hg (see fig. 2) is shown in part 3 of figure 3. It will be seen that the values for the refractive indices of the fractions which constituted the last 20 to 25 percent of the charge approach the value for the refractive index of 1-methyl-5,6,7,8-tetrahydronaphthalene. The fractions with indices from 1.534 to 1.542 froze readily at from  $-45$  to  $-25^{\circ}$  C and were segregated as 1-methyl-5,6,7,8-tetrahydronaphthalene concentrates. The material of lower refractive index was redistilled azeotropically, and as much of the 1-methyl-5,6,7,8-tetrahydronaphthalene concentrates segregated as was practical.

### 4. SEPARATION OF 2-METHYLNAPHTHALENE

From the very high refractive indices of the material distilling in the region from  $144^{\circ}$  to  $148^{\circ}$  C at 56.8 mm Hg (see fig. 2), together with the fact that this was the region from which a substantial quantity of 2-methylnaphthalene had been separated in the previous investigation [1], it was obvious that these fractions still contained some 2-methylnaphthalene. As can be seen from part 4 of figure 3, an

excellent separation of this hydrocarbon is obtained by a single azeotropic distillation. In this distillation the percentage of oil in the distillate fractions decreases to less than 1 percent by volume as the hydrocarbon portion of the material remaining undistilled approaches 2-methylnaphthalene in composition. It is then unprofitable to continue the distillation further. The refractive indices shown in part 4 of figure 3 therefore refer to the oil obtained from the distillate fractions up to about 64 percent recovered, while the refractive index of the remainder refers to oil recovered from the residue. The oil from the residue which had a refractive index close to that of 2-methylnaphthalene, and which crystallized at 30° C (compare with 34.44° C for the freezing point of pure 2-methylnaphthalene), was segregated as 2-methylnaphthalene.

Besides the 2-methylnaphthalene actually separated by azeotropic distillation in the manner described, an additional quantity, which came from the comparatively small volume distilling in the region 148° to 150° C at 56.8 mm Hg (see fig. 2), was allocated to this compound. This material was substantially a mixture of 1- and 2-methylnaphthalenes and was allocated equally to these compounds (see section VI and table 6).

#### 5. SEPARATION OF 1-METHYLNAPHTHALENE

The fractions distilling from 150° to 151° C (see fig. 2) had refractive indices ( $n_D^{25}$ ) of 1.608 to 1.612. This material consisted substantially of 1-methylnaphthalene and was not separated further. In addition to this quantity, half the volume distilling from 148° to 150° C at 56.8 mm Hg was allocated to this compound (see section VI and table 6), as described in the preceding paragraph.

It may be pointed out that a mixture of 1- and 2-methylnaphthalenes may be obtained from crude petroleum in a very simple manner. It is necessary only to distill the kerosene fraction (or that portion containing the 1- and 2-methylnaphthalenes) in an efficient column, and then to select and distill azeotropically the narrow-boiling portion in which these two compounds are contained. In the azeotropic distillation, paraffins, naphthenes, alkylbenzenes, homologs of tetrahydronaphthalene, and a mixture of the 1- and 2-methylnaphthalenes will distill in the order mentioned. Thus the last fractions from the distillation, or the residue, will contain the 1- and 2-methylnaphthalenes, which can then be separated from one another as previously described [1].

#### V. PURIFICATION, IDENTITY, AND PHYSICAL PROPERTIES OF THE PURIFIED HYDROCARBONS

The purification of the individual hydrocarbons was accomplished by repeated fractional crystallization, using as starting material the concentrates whose separation has been described. 5,6,7,8-Tetrahydronaphthalene and its 1- and 2-methyl homologs were crystallized from solutions containing approximately 50 percent by volume of dichlorodifluoromethane. Owing to the relatively high freezing point (-6.25° C) of 1,2,3,4-tetramethylbenzene, dichlorodifluoromethane could not be used as a solvent in the final stages of purification of this compound. It was therefore crystallized from a solution containing



approximately 50 percent by volume of *n*-pentane. The purification processes were followed by measurements of the refractive index and occasionally by determinations of the freezing point.

Owing to the fragmentary and unreliable nature of the data on the physical properties of 5,6,7,8-tetrahydronaphthalene and its 1- and 2-methyl homologs (no data appear to have been published on 1-methyl-5,6,7,8-tetrahydronaphthalene), synthetic samples of these three hydrocarbons were obtained and purified.

Eastman's 5,6,7,8-tetrahydronaphthalene was used as the source for this substance. The "best" sample of this material was obtained after five crystallizations performed in the same manner as with the material from petroleum.

The synthetic samples of the 1- and 2-methyl-5,6,7,8-tetrahydronaphthalenes were obtained from N. L. Drake of the University of Maryland, who kindly prepared them by methods which left no doubt as to their identity. The 1-methyl-5,6,7,8-tetrahydronaphthalene, of which 131 ml was available, was distilled azeotropically with diethylene glycol monomethyl ether in the same manner as described for the material from petroleum.<sup>7</sup> Six fractions of hydrocarbon material, with a total volume of 83 ml and with refractive indices ( $n_D^{25}$ ) between 1.5419 and 1.5423, taken from the middle of the distillate, were combined and crystallized once from dichlorodifluoromethane to obtain a "best" sample.

The 2-methyl-5,6,7,8-tetrahydronaphthalene, of which only 85 ml was available, was purified by azeotropic distillation and by a single crystallization of the best fractions from the distillate. Owing to the small amount of material, it was possible to obtain a "best" sample of only 32 ml. The purity of this sample was not high, but was sufficient for purposes of identification.

The "best" sample of each hydrocarbon, both the synthetic and that from petroleum, was distilled at a low pressure so that it was not heated above 60° to 70° C, and a small residue was discarded. The distillate was used for the determination of the physical properties.

The amounts of impurity in the best samples, as well as values of the freezing points for material with zero impurity, were estimated from time-temperature freezing and melting curves according to the procedure described previously [4]. In the case of 1,2,3,4-tetramethylbenzene and 5,6,7,8-tetrahydronaphthalene it was possible to estimate the amount of impurity from the freezing curve. However, in the case of 1-methyl-5,6,7,8-tetrahydronaphthalene and 2-methyl-5,6,7,8-tetrahydronaphthalene the recovery from undercooling is extremely slow, and the freezing curves can not be used to determine the freezing point and estimate the amount of impurity. Instead, the freezing point and amount of impurity were determined from melting curves. The curves given in figure 4 illustrate this behavior for 2-methyl-5,6,7,8-tetrahydronaphthalene. In this figure the dashed lines represent the extrapolation necessary to determine the freezing point. The nearly vertical dashed line is an extrapolation of the liquid warming curve from a point above which it was certain that all the sample was in the liquid phase. There is also indicated by the value 0.083° C the difference in temperature of thermodynamic

<sup>7</sup> The distillation of such a small quantity of material in a large column was feasible only by the use of an azeotrope-forming substance which greatly increased the volume of distillate. (See reference [3]).

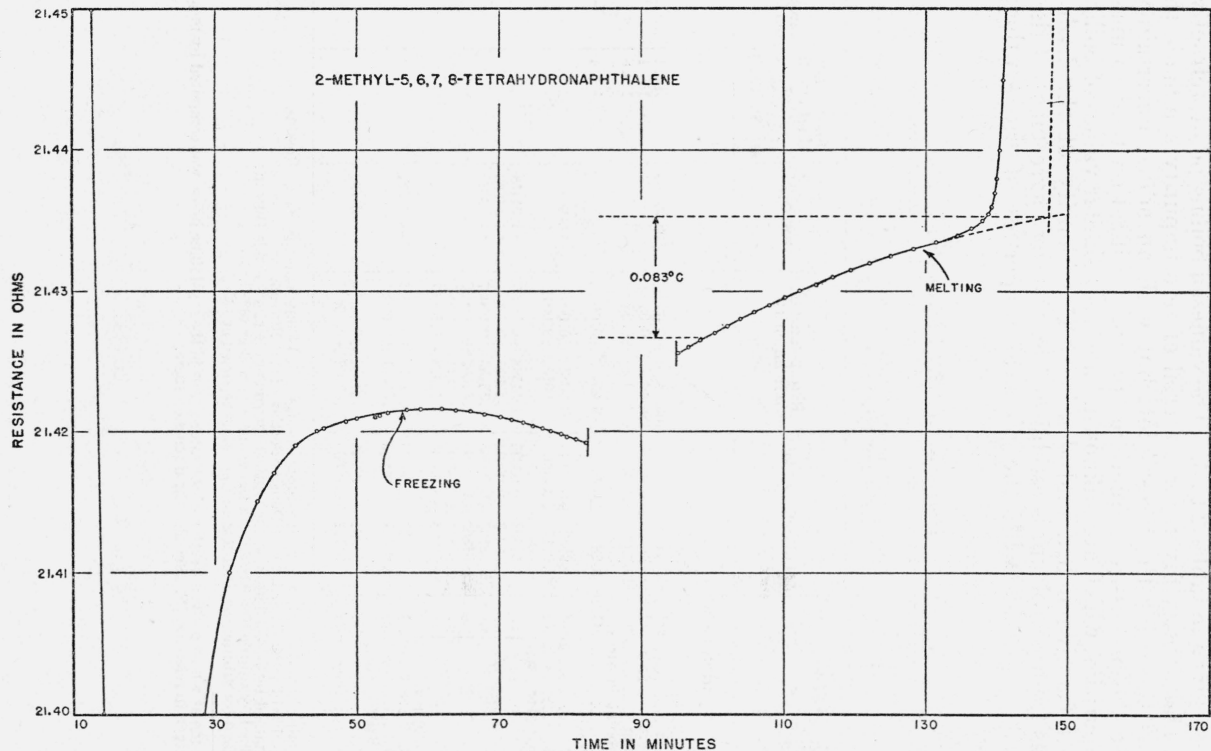


FIGURE 4.—Portions of time-temperature freezing and melting curves for 2-methyl-5,6,7,8-tetrahydronaphthalene.



equilibrium between the states having one-third and zero fraction of the substance in the crystalline phase.<sup>8</sup>

The properties of the best samples, both the synthetic ones and those from petroleum, together with values from previous investigations, are given in tables 2 to 5. The values of boiling point, refractive index, and density given for material of zero impurity are made the same as those for the "best" lot, but with an added uncertainty, because the processes of fractionation and purification tend to make the impurities, which are unknown, have very similar values of boiling point, refractive index, and density. The identity of the hydrocarbons from petroleum is established by the close agreement of their physical properties with the physical properties of the synthetic sample.

TABLE 2.—*Properties of 1,2,3,4-tetramethylbenzene*

Properties	Values from this investigation (material from petroleum)		Values from previous investigations		
	Actual "best" lot	Extrapolated to zero impurity	Auwers [5]	Smith and MacDougall [6] or MacDougall and Smith [7]	Jacobson [8]
Amount of impurity, mole fraction	0.00058 ± 0.00006	0			
Boiling point <sup>a</sup> at:					
760 mm.....°C	205.04 ± 0.03	205.04 ± 0.03	203 to 204	204.4	204
217.2 mm.....°C	158.46 ± 0.03	158.46 ± 0.03		158.1	
57.3 mm.....°C	119.40 ± 0.05	119.40 ± 0.05		119.8	
Freezing point in air at 1 atm.....°C	-6.28 ± 0.01	-6.25 ± 0.01		-6.4	-4
Density <sup>b</sup> at:			d 0.9014		
20° C.....g/ml	0.9053 ± 0.0001	0.9053 ± 0.0001			
25° C.....g/ml	.9015 ± 0.0001	.9015 ± 0.0001			
Refractive index <sup>c</sup> at:				• 1.51458 • 1.51868 • 1.53029	
20° C.....	{ <i>n<sub>c</sub></i> .....	1.51563 ± 0.00005	1.51563 ± 0.00007		
	{ <i>n<sub>D</sub></i> .....	1.52013 ± 0.00005	1.52013 ± 0.00007		
	{ <i>n<sub>F</sub></i> .....	1.53133 ± 0.00005	1.53133 ± 0.00007		
25° C.....	{ <i>n<sub>c</sub></i> .....	1.51362 ± 0.00005	1.51362 ± 0.00007		
	{ <i>n<sub>D</sub></i> .....	1.51811 ± 0.00005	1.51811 ± 0.00007		
	{ <i>n<sub>F</sub></i> .....	1.52923 ± 0.00005	1.52923 ± 0.00007		
Refractive dispersion at:			0.01571		
20° C.....( <i>n<sub>F</sub></i> - <i>n<sub>c</sub></i> )	0.01570 ± 0.00005	0.01570 ± 0.00005			
25° C.....( <i>n<sub>F</sub></i> - <i>n<sub>c</sub></i> )	.01561 ± 0.00005	.01561 ± 0.00005			
Specific dispersion at:			.01736		
20° C.....( <i>n<sub>F</sub></i> - <i>n<sub>c</sub></i> )/ <i>d</i>	.01734 ± 0.00005	.01734 ± 0.00005			
25° C.....( <i>n<sub>F</sub></i> - <i>n<sub>c</sub></i> )/ <i>d</i>	.01732 ± 0.00005	.01732 ± 0.00005			

<sup>a</sup> Determined by B. J. Mair with the apparatus of C. B. Willingham and F. D. Rossini.

<sup>b</sup> Determined by the Capacity and Density Section of this Bureau.

<sup>c</sup> Determined by L. W. Tilton, of the Optical Instrument Section of this Bureau.

<sup>d</sup> Obtained by subtracting 0.0030 from the values reported at 16° C.

<sup>e</sup> Obtained by subtracting 0.00163 from the values reported at 16° C.

<sup>8</sup> The time at which a given fraction of the sample was in the crystalline phase was computed by means of eq 28 given in reference [4]. See also the discussion there.

TABLE 3.—Properties of 5,6,7,8-tetrahydronaphthalene

Properties	Values from this investigation				Values from previous investigations *		
	Material from petroleum		Purified synthetic material		Herz and Schufran [9]	Auwers [10]	Adkins and Reid [11]
	Actual "best" lot	Extrapolated to zero impurity	Actual "best" lot	Extrapolated to zero impurity			
Amount of impurity, mole fraction.....	0.015 ±0.002	0	0.0057 ±0.0008	0			
Boiling point <sup>a</sup> at:							
760 mm..... °C	207.66 ±0.10		207.57 ±0.10	207.57 ±0.10	207.3		
217.2 mm..... °C			159.97 ±0.10	159.97 ±0.10	159.3		
57.3 mm..... °C			120.21 ±0.10	120.21 ±0.10	119.2		
Freezing point in air at 1 atm..... °C	-36.22 ±0.01	-35.79 ±0.03	-35.97 ±0.01	-35.80 ±0.02	-35.0		
Density <sup>b</sup> at:							
20° C..... g/ml	0.9705 ±0.0001		0.9702 ±0.0001	0.9702 ±0.0002	0.9693	0.971	
25° C..... g/ml	.9665 ±0.0001		.9662 ±0.0001	.9662 ±0.0002	.9655		
Refractive index <sup>c</sup> at:							
20° C.....							
..... <i>n<sub>C</sub></i>	1.53703 ±0.00005		1.53676 ±0.00005	1.53676 ±0.00015		d 1.53826	
..... <i>n<sub>D</sub></i>	1.54161 ±0.00005		1.54135 ±0.00005	1.54135 ±0.00015		d 1.54283	
..... <i>n<sub>F</sub></i>	1.55326 ±0.00005		1.55291 ±0.00005	1.55291 ±0.00015		d 1.55466	
25° C.....							1.5395
..... <i>n<sub>C</sub></i>	1.53496 ±0.00005		1.53466 ±0.00005	1.53466 ±0.00015			
..... <i>n<sub>D</sub></i>	1.53952 ±0.00005		1.53919 ±0.00005	1.53919 ±0.00015			
..... <i>n<sub>F</sub></i>	1.55097 ±0.00005		1.55065 ±0.00005	1.55065 ±0.00015			
Refractive dispersion at:							
20° C..... ( <i>n<sub>F</sub></i> - <i>n<sub>C</sub></i> )	.01623 ±0.00005		.01615 ±0.00005	.01615 ±0.00010		0.01640	
25° C..... ( <i>n<sub>F</sub></i> - <i>n<sub>C</sub></i> )	.01601 ±0.00005		.01599 ±0.00005	.01599 ±0.00010			
Specific dispersion at:							
20° C..... ( <i>n<sub>F</sub></i> - <i>n<sub>C</sub></i> )/ <i>d</i>	.01672 ±0.00005		.01665 ±0.00005	.01665 ±0.00010		0.01689	
25° C..... ( <i>n<sub>F</sub></i> - <i>n<sub>C</sub></i> )/ <i>d</i>	.01656 ±0.00005		.01655 ±0.00005	.01655 ±0.00010			

<sup>a</sup> Determined by B. J. Mair with the apparatus of C. B. Willingham and F. D. Rossini.

<sup>b</sup> Determined by the Capacity and Density Section of this Bureau.

<sup>c</sup> Determined by L. W. Tilton, of the Optical Instruments Section of this Bureau.

<sup>d</sup> Auwers [10] gives sets of values on three samples which differ substantially among themselves. These values were obtained by subtracting 0.00061 from the lowest set of values reported by Auwers at 21.4° C.

\* See also references [14], [15], [16], and [17].

TABLE 4.—*Properties of 2-methyl-5, 6, 7, 8-tetrahydronaphthalene*

Properties	Values from this investigation				Values from previous investigations
	Material from petroleum		Purified synthetic material		
	Actual "best" lot	Extrapolated to zero impurity	Actual "best" lot	Krollpfeifer and Schäfer [12]	
Amount of impurity, mole fraction.....	0.0046 ±0.0007	0	0.031 ±0.004		
Boiling point <sup>a</sup> at:					
760 mm.....°C.....	229.03 ±0.05	229.03 ±0.05	229.06 ±0.05	224 to 226	
217.2 mm.....°C.....	179.91 ±0.05	179.91 ±0.05			
57.3 mm.....°C.....	138.75 ±0.07	138.75 ±0.07			
Freezing point in air at 1 atm.....°C.....	-39.92 ±0.01	-39.75 ±0.03	-40.84 ±0.03		
Density <sup>c</sup> at:					
20° C.....g/ml.....	0.9537 ±0.0001	0.9537 ±0.0002	0.9543 ±0.0001	d 0.9504	
25° C.....g/ml.....	.9500 ±0.0001	.9500 ±0.0002	.9505 ±0.0001		
Refractive index <sup>e</sup> at:					
20° C..... $\left\{ \begin{array}{l} n_c \\ n_D \\ n_F \end{array} \right.$ .....	1.53115 ±0.00005 1.53572 ±0.00005 1.54706 ±0.00005	1.53115 ±0.00010 1.53572 ±0.00010 1.54706 ±0.00010	1.53107 ±0.00005 1.53571 ±0.00005 1.54697 ±0.00005	• 1.53118 • 1.53521 • 1.54709	
25° C..... $\left\{ \begin{array}{l} n_c \\ n_D \\ n_F \end{array} \right.$ .....	1.52920 ±0.00005 1.53365 ±0.00005 1.54498 ±0.00005	1.52920 ±0.00010 1.53365 ±0.00010 1.54498 ±0.00010	1.52914 ±0.00005 1.53361 ±0.00005 1.54499 ±0.00005		
Refractive dispersion at:					
20° C..... $(n_F - n_C)$ .....	0.01591 ±0.00005	0.01591 ±0.00005	0.01590 ±0.00005	0.01591	
25° C..... $(n_F - n_C)$ .....	.01578 ±0.00005	.01579 ±0.00005	.01585 ±0.00005		
Specific dispersion at:					
20° C..... $(n_F - n_C)/d$ .....	.01668 ±0.00005	.01668 ±0.00005	.01666 ±0.00005	.01674	
25° C..... $(n_F - n_C)/d$ .....	.01661 ±0.00005	.01662 ±0.00005	.01668 ±0.00005		

<sup>a</sup> Determined by B. J. Mair with the apparatus of C. B. Willingham and F. D. Rossini.

<sup>b</sup> Determined by the Capacity and Density Section of this Bureau.

<sup>c</sup> Determined by L. W. Tilton, of the Optical Instruments Section of this Bureau.

<sup>d</sup> Obtained by subtracting 0.0037 from the value reported at 15.1° C.

<sup>e</sup> Obtained by subtracting 0.00198 from the values reported at 15.1° C.

TABLE 5.—*Properties of 1-methyl-5, 6, 7, 8-tetrahydronaphthalene*

Properties	Values from this investigation			
	Material from petroleum		Purified synthetic material	
	Actual "best" lot	Extrapolated to zero impurity	Actual "best" lot	Extrapolated to zero impurity
Amount of impurity, mole fraction.....	0.0029 ±0.0004	0	0.0034 ±0.0005	0
Boiling point <sup>a</sup> at:				
760 mm.....°C.....	234.35 ±0.05	234.35 ±0.05	234.39 ±0.05	
217.2 mm.....°C.....	184.98 ±0.05	184.98 ±0.05		
57.3 mm.....°C.....	143.76 ±0.07	143.76 ±0.07		
Freezing point in air at 1 atm.....°C.....	-23.02 ±0.01	-22.90 ±0.03	-23.04 ±0.01	-22.95 ±0.04
Density <sup>b</sup> at:				
20° C.....g/ml.....	0.9720 ±0.0001	0.9720 ±0.0002	0.9720 ±0.0001	
25° C.....g/ml.....	.9682 ±0.0001	.9682 ±0.0002	.9683 ±0.0001	
Refractive index <sup>e</sup> at:				
20° C..... $\left\{ \begin{array}{l} n_c \\ n_D \\ n_F \end{array} \right.$ .....	1.53937 ±0.00005 1.54395 ±0.00005 1.55536 ±0.00005	1.53937 ±0.00010 1.54395 ±0.00010 1.55536 ±0.00010	1.53935 ±0.00005 1.54397 ±0.00005 1.55527 ±0.00005	
25° C..... $\left\{ \begin{array}{l} n_c \\ n_D \\ n_F \end{array} \right.$ .....	1.53738 ±0.00005 1.54190 ±0.00005 1.55325 ±0.00005	1.53738 ±0.00010 1.54190 ±0.00010 1.55325 ±0.00010	1.53735 ±0.00005 1.54188 ±0.00005 1.55324 ±0.00005	
Refractive dispersion at:				
20° C..... $(n_F - n_C)$ .....	0.01599 ±0.00005	0.01597 ±0.00005	0.01592 ±0.00005	
25° C..... $(n_F - n_C)$ .....	.01587 ±0.00005	.01588 ±0.00005	.01589 ±0.00005	
Specific dispersion at:				
20° C..... $(n_F - n_C)/d$ .....	.01645 ±0.00005	.01645 ±0.00005	.01638 ±0.00005	
25° C..... $(n_F - n_C)/d$ .....	.01639 ±0.00005	.01639 ±0.00005	.01641 ±0.00005	

<sup>a</sup> Determined by B. J. Mair with the apparatus of C. B. Willingham and F. D. Rossini.

<sup>b</sup> Determined by the Capacity and Density Section of this Bureau.

<sup>c</sup> Determined by L. W. Tilton, of the Optical Instruments Section of this Bureau.

## VI. SUMMARY OF AMOUNTS OF MATERIAL PROCESSED, LOSSES DURING PROCESSING, AND AMOUNTS OF HYDROCARBONS ISOLATED

In table 6 is given a summary of the material processed, the losses during processing, and the amounts of the individual hydrocarbons separated. For an explanation of a similar table, together with a description of the method used in allocating the losses and in computing the percentages of the hydrocarbons isolated, the reader is referred to the preceding publication [1]. The ninth column of table 6 gives the total amount of the given hydrocarbon isolated, and the tenth column gives the total amount of the hydrocarbon estimated to be present in the petroleum. In both columns the values are in percentage, based on the original distillate, 114° to 144° C at 56.8 mm Hg, as 100 percent. There are included in this table values for the amounts of naphthalene in this petroleum taken from the preceding publication [1]. The total amount of the seven aromatic hydrocarbons actually determined to date as individual compounds amounts to 5.32 percent of the distillate from 114° to 144° C at 56.8 mm Hg and 27.8 percent of all the aromatic material in this same distillate. The corresponding values for the total amount of these seven compounds estimated to be present are 5.76 percent and 30.1 percent, respectively.

TABLE 6.—*Summary of the material processed, losses due to processing, and amounts of hydrocarbons isolated*

Material	Volume	Process	Material lost in process		Product	Amount of the product or of the given hydrocarbons separated	Amount of the hydrocarbon previously separated [1]	Total amount of the given hydrocarbon isolated <sup>a</sup>	Estimated total amount of the given hydrocarbon in the petroleum
			Volume						
	<i>Liters</i>		<i>Liters</i>	<i>Percent</i>		Percentage of the distillate 114° to 144° C (at 56.8 mm Hg)	Percentage of the distillate 114° to 144° C (at 56.8 mm Hg)	Percentage of the distillate 114° to 144° C (at 56.8 mm Hg)	Percentage of the distillate 114° to 144° C (at 56.8 mm Hg)
Aromatic distillate (118° to 120.5° C at 56.8 mm Hg).	} 3.768	{ Azeotropic distillation and crystallization.	} 0.824	21.9	1,2,3,4-Tetramethylbenzene.....	1.01	-----	1.01	1.06±0.07
					5,6,7,8-Tetrahydronaphthalene.....	0.24	-----	0.24	0.27±0.03
					Unresolved material (high index).....	.04	-----	-----	-----
					Unresolved material (low index).....	1.87	-----	-----	-----
Aromatic distillate (137° to 140° C at 56.8 mm Hg).	} 2.564	{ Azeotropic distillation.	} .505	19.7	2-Methyl-5,6,7,8-tetrahydronaphthalene.....	0.62	-----	.62	.68±0.06
					Unresolved material (high index).....	.11	-----	-----	-----
					Unresolved material (low index).....	1.41	-----	-----	-----
					1-Methyl-5,6,7,8-tetrahydronaphthalene.....	0.40	-----	.40	.65±0.12
Aromatic distillate (141° to 144° C at 56.8 mm Hg).	} 2.050	{ Azeotropic distillation.	} .228	11.1	Unresolved material (high index).....	.07	-----	-----	-----
					Unresolved material (low index).....	1.24	-----	-----	-----
					Unresolved material (low index).....	0.81	-----	-----	-----
					2-Methylnaphthalene.....	.40	1.28	1.80	1.80±0.10
Aromatic distillate (148° to 150° C at 56.8 mm Hg).	} 0.252	-----	-----	-----	2-Methylnaphthalene.....	.12	-----	-----	-----
					1-Methylnaphthalene.....	.12	0.35	0.84	0.84±0.06
Aromatic distillate (150° to 151° C at 56.8 mm Hg).	} .364	-----	-----	-----	1-Methylnaphthalene.....	.37	-----	-----	-----
					Naphthalene.....	-----	.41	.41	.46±0.04

<sup>a</sup> The losses occurring in each process of fractionation were charged equally on a fractional basis to the products obtained from the given process. In this way, the total material actually on hand, regardless of the losses which occurred, represent the original distillate 114° to 144° C at 56.8 mm Hg (see reference [1]).

## VII. PREVIOUS INVESTIGATIONS

Of the four hydrocarbons, 1,2,3,4-tetramethylbenzene, 5,6,7,8-tetrahydronaphthalene, 1-methyl-5,6,7,8-tetrahydronaphthalene, and 2-methyl-5,6,7,8-tetrahydronaphthalene, whose isolation is described here, none, as far as the authors are aware, has been isolated previously from petroleum. However, Nenitzescu, Isacescu, and Isopescu [13], using the aromatic fractions from a Gura Ocnitei oil, concluded, from combustion analyses of fractions which distilled between 204° and 205° C at atmospheric pressure, that these fractions contained 1,2,3,4-tetramethylbenzene. As additional evidence supporting this conclusion, these authors prepared a bromide from these fractions with a melting point which agreed with the melting point of 5,6-dibromo-1,2,3,4-tetramethylbenzene. Ross and Leather [18] treated a fraction of a Borneo oil, which distilled in the neighborhood of 200° C, with fuming nitric acid and obtained a nitro compound which, on the basis of combustion analyses, they believed to be dinitrotetrahydronaphthalene.

## VIII. REFERENCES

- [1] B. J. Mair and A. J. Streiff, *J. Research NBS* **24**, 395 (1940) RP1289.
- [2] F. D. Rossini and C. B. Willingham (work not yet published).
- [3] B. J. Mair, A. R. Glasgow, and F. D. Rossini, *J. Research NBS* **27**, 39 (1941) RP1402.
- [4] B. J. Mair, A. R. Glasgow, and F. D. Rossini, *J. Research NBS* **26**, 591 (1941) RP1397.
- [5] K. v Auwers, *Liebigs Ann. Chem.* **419**, 92 (1919).
- [6] L. I. Smith and F. H. MacDougall, *J. Am. Chem. Soc.* **51**, 3001 (1929).
- [7] F. H. MacDougall and L. I. Smith, *J. Am. Chem. Soc.* **52**, 1998 (1930).
- [8] O. Jacobsen, *Ber. deut. chem. Ges.* **19**, 1213, 2514 (1886).
- [9] W. Herz and P. Schuftan, *Z. physik Chem.* **101**, 269 (1922).
- [10] K. v Auwers, *Ber. deut. chem. Ges.* **46**, 2988 (1913).
- [11] H. Adkins and W. A. Reid, *J. Am. Chem. Soc.* **63**, 742 (1941).
- [12] F. Krollpfeiffer and W. Schäfer, *Ber. deut. chem. Ges.* **56B**, 620 (1923).
- [13] C. D. Nenitzescu, D. A. Isacescu, and A. C. Isopescu, *Österr. chem. Ztg.* **42**, 350 (1939).
- [14] H. Brücker, *Gas u Wasserfach* **75**, 573 (1932).
- [15] G. Schroeter, *Liebigs Ann. Chem.* **426**, 1 (1922).
- [16] W. A. Roth and K. v. Auwers, *Liebigs Ann. Chem.* **407**, 145 (1915).
- [17] F. Krollpfeiffer, *Liebigs Ann. Chem.* **430**, 161 (1923).
- [18] R. Ross and J. P. Leather, *Analyst* **31**, 284 (1906).

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