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PHYSICAL PROPERTIES OF SOME PURIFIED ALIPHATIC HYDROCARBONS

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ABSTRACT

In an investigation of the suitability of various paraffin hydrocarbons as constituents of aviation fuel, which is being conducted for the National Advisory Committee for Aeronautics, the Navy Bureau of Aeronautics, and the Army Air Corps, four olefin and seven paraffin hydrocarbons have been obtained in a state of high purity. Eight of these materials were synthesized, one was isolated from a commercial synthetic crude, and two were obtained from commercial sources. All were purified by distillation in automatically controlled fractionating columns of high efficiency.

The measured physical properties of these materials included freezing point, boiling point and its variation with pressure, refractive index and density and their variations with temperature.

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I. INTRODUCTION

The materials described herein were prepared in connection with an investigation of the suitability of various paraffin hydrocarbons as constituents of aviation fuel. This investigation is being conducted at the National Bureau of Standards for the National Advisory Committee for Aeronautics, the Navy Bureau of Aeronautics, and the Army Air Corps. In the previous paper [1]¹ of this series, the preparation and properties of purified 2,2,3-trimethylpentane were described.

Eight of the hydrocarbons described herein were synthesized, one was isolated by fractionation from a commercial synthetic crude, and two were obtained from commercial sources. All of these materials were further purified by distillation in automatically controlled fractionating columns of high efficiency.

¹ Figures in brackets indicate the literature references at the end of this paper.

II. FRACTIONATING COLUMNS

The high purity of the compounds described in this paper resulted primarily from the efficiency of the two fractionating columns used for the final purification. Both columns operate automatically and continuously throughout a distillation, whether it takes 4 days or 4 weeks.

Both columns are built entirely of Pyrex glass. The smaller is a 150-plate bubble-cap column, the fractionating elements of which follow the design of Bruun [2]. The other column is a 600- by 4-cm helix-packed column. Both columns have silvered vacuum jackets, heating elements wound around the latter, and 1 inch of asbestos insulation outside the heating elements. Five-liter still-pots are sealed on the columns. The head of each column has a thermometer well. The columns operate under total reflux with intermittent sampling automatically timed.

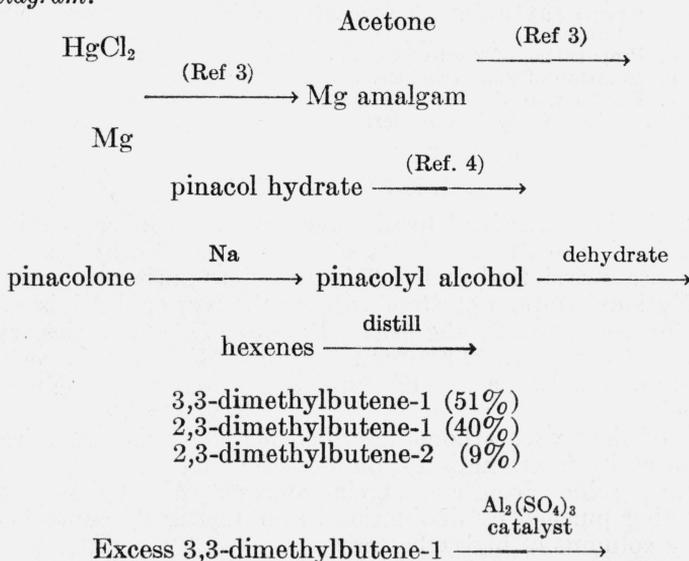
Other columns similar to the bubble-cap have shown efficiencies of over 80 theoretical plates for a 120-plate column; therefore, it is believed the efficiency of the 150-plate bubble-cap column is close to 100 theoretical plates. By comparison of the distillation of the same or similar materials in the two columns, it was evident that the 600- by 4-cm packed column was more efficient than the bubble-cap column.

The criteria which guided the selection of samples for measurement of physical properties were the constancy of boiling point and the refractive index of the fractions, and other factors of the particular run which experience had shown might affect the purity of the fraction.

III. PREPARATION OF MATERIALS

1. PREPARATION OF 3,3-DIMETHYLBUTENE-1, 2,3-DIMETHYLBUTENE-1, AND 2,3-DIMETHYLBUTENE-2

Flow diagram:



- 3,3-dimethylbutene-1 (7%)
- 2,3-dimethylbutene-1 (28%)
- 2,3-dimethylbutene-2 (65%)

A. *Pinacol hydrate*.—Pinacol hydrate was prepared from acetone and magnesium amalgam by a modification of the procedure given in *Organic Syntheses* [3].

A 5-liter three-necked flask was fitted with a 500-ml dropping funnel and a 150- by 2-cm condenser in the two smaller necks. Water at 5° to 10°C was circulated through the condenser jacket. The large center neck was stoppered with a cork. In the flask were placed 120 g of magnesium turnings and 500 ml of benzene.

(Technical benzene and acetone for this preparation were dried for 2 days over calcium chloride and decanted. No increase in yield was found when these materials were further purified.) A solution of 135 g of mercuric chloride in 260 ml of acetone was added all at once, and the very vigorous reaction controlled by adding portions of 700 ml of benzene as needed. In this way all the magnesium was amalgamated equally before the magnesium pinacolate had swelled up to the point where addition of mercuric chloride caused local amalgamation and separation of free mercury. After the benzene had been added, 500 ml of acetone was added slowly, and then a solution of 300 ml of benzene and 390 ml of acetone was added. The swollen magnesium pinacolate was worked down to the bottom of the flask, when necessary, by inserting a wooden paddle in the large neck of the flask and stirring. The product was worked up in the way described in *Organic Syntheses* [3]. Concentration of the pinacol hydrate solution was effected by distillation from a 12-liter flask heated internally with a steam coil. The vapors were condensed by passing through a 1/2-in. copper-coil water-cooled condenser. The yield of crude pinacol hydrate was 52 to 58 percent of the calculated amount based on magnesium. About 50 kg was prepared.

B. *Pinacolone*.—Pinacolone was prepared in 70-percent yield from pinacol hydrate by the method described in *Organic Syntheses* [4]. Double quantities were used, and the reaction was carried out in a 5-liter three-necked flask.

The crude pinacolone was distilled through a 100- by 2-cm column packed with Pyrex helices. Distillate representing 80 to 83 percent of the charge was collected between 105° and 106°C.

C. *Pinacolyl alcohol*.—A 12-liter round-bottomed flask was fitted with a 150- by 2-cm condenser cooled with water at 5° to 10°C. The flask was charged with 740 ml (6 moles) of purified pinacolone, 3,600 ml of ether and 2,700 ml of saturated sodium carbonate solution. Sodium (690 g, 30 moles) cut into small pieces was added through the condenser as fast as possible without causing an excessively violent reaction. This required from 6 to 7 hours. When sodium carbonate crystallized out to such an extent that the mixing caused by evolution of hydrogen was impaired, water was added, 25 ml at a time, until the salt was just dissolved.

When the reaction was complete, the layers were separated, the aqueous layer extracted once with 1,000 ml of ether, and the combined ether solutions were washed with water, dried with potassium carbonate, and distilled through a 100- by 2-cm packed column. The product collected boiled at 120° to 122° C. In this way 10,850 ml of pinacolyl

alcohol was prepared from 12,295 ml of pinacolone (88.4 percent of the calculated yield).

D. Dehydration of pinacolyl alcohol.—Pinacolyl alcohol was dehydrated by passing it through a 100- by 2-cm horizontal Pyrex-glass tube electrically heated, well lagged, and filled with alumina (Hydralo, from J. T. Baker Chemical Co.). The alcohol was added at the rate of 60 ml per hour while the tube was maintained at 297° to 305° C. The products, olefins and water, were separated, and the olefins dried

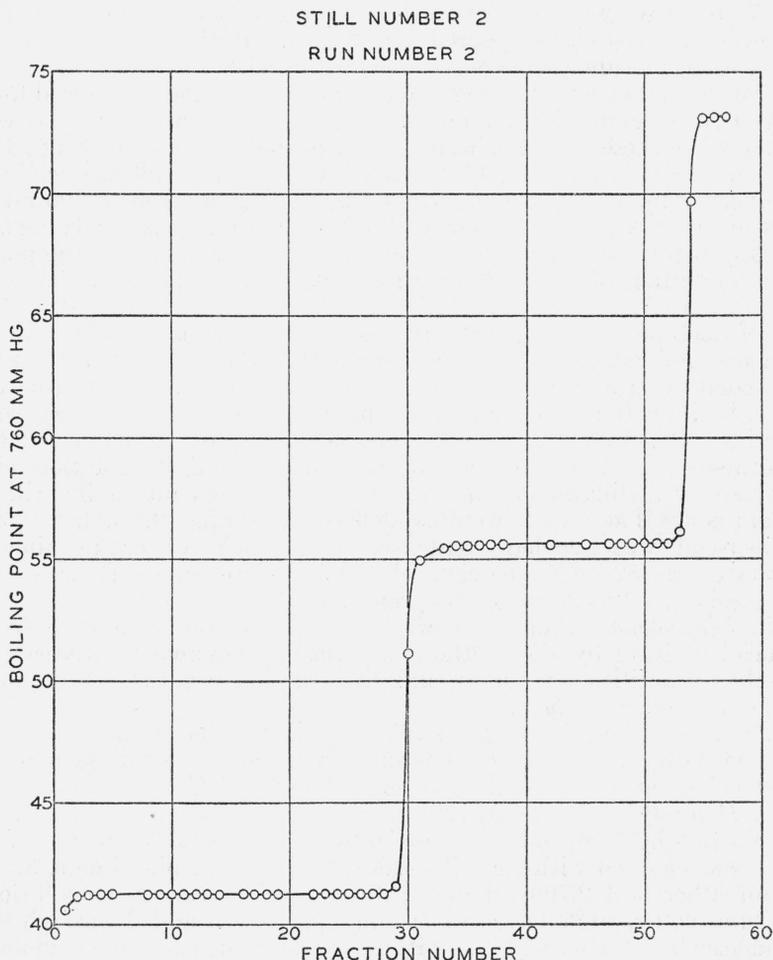


FIGURE 1.—*Fractional distillation of dimethylbutenes.*

with anhydrous sodium sulfate. In this way 7,742 ml of mixed olefins was obtained from 7,795 ml of the alcohol. The product was water-white and contained no alcohol. The mixture of olefins was distilled through the 150-plate bubble-cap column. One charge, the distillation curve of which is shown in figure 1, was separated into 57 fractions, 27 of which boiled between 41.23° and 41.24° C (head temperatures), 21 between 55.56° and 55.62° C, and 5 between 73.17°

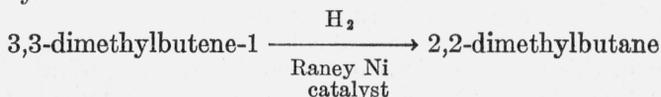
and 73.18° C. Not including the holdup (210 ml, 3½ fractions) and four intermediate fractions, this represents 51.0 percent of 3,3-dimethylbutene-1, 39.6 percent of 2,3-dimethylbutene-1, and 9.4 percent of 2,3-dimethylbutene-2.

Since approximately equal portions of the three olefins were desired, excess 3,3-dimethylbutene-1 and intermediate fractions were passed through the catalyst tube previously described, filled with aluminum sulfate maintained at 280° to 290° C. The first portion of the effluent contained hydrogen sulfide and sulfur, but the remainder was clean. All olefins from the reaction were washed with sodium plumbite and shaken with mercury. From 3,570 ml charged, there was obtained 3,390 ml of mixed olefins. The relative proportions, as determined by distillation analysis, were: 3,3-dimethylbutene-1, 7 percent; 2,3-dimethylbutene-1, 28 percent; and 2,3-dimethylbutene-2, 65 percent. These results substantiate those found by Cramer and Glasebrook [5].

Appropriate fractions from several runs were combined and redistilled, and samples of the middle portion of each distillate were used in the determination of physical constants.

2. PREPARATION OF 2,2-DIMETHYLBUTANE

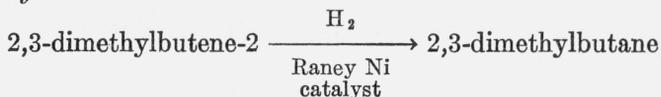
Flow diagram:



Fifteen hundred milliliters of 3,3-dimethylbutene-1 was hydrogenated at 1,500 lb/in.² pressure, at 150° C, in the presence of Raney nickel catalyst. After washing, drying, and refluxing over sodium, 1,485 ml was carefully fractionated in the 600- by 4-cm packed column.

3. PREPARATION OF 2,3-DIMETHYLBUTANE

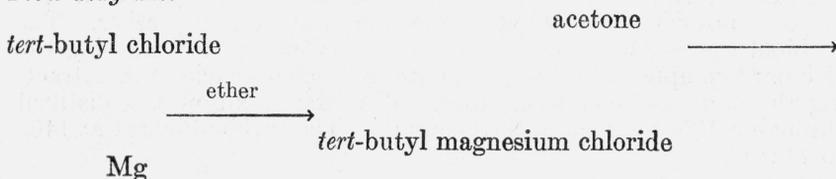
Flow diagram:

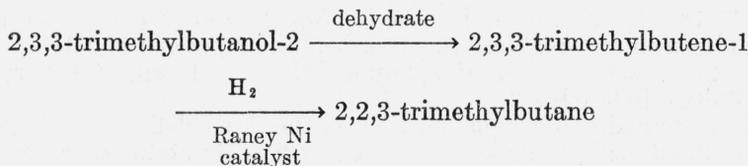


One thousand milliliters of constant-boiling 2,3-dimethylbutene-2 was hydrogenated at 1,800 lb/in.² pressure, at 130° C, in the presence of Raney nickel catalyst. The product was washed, dried, refluxed over sodium, and distilled in the manner already described. The product, 987 ml, was carefully fractionated in the 600- by 4-cm packed column.

4. PREPARATION OF 2,3,3-TRIMETHYLBUTENE-1 AND 2,2,3-TRIMETHYLBUTANE

Flow diagram:





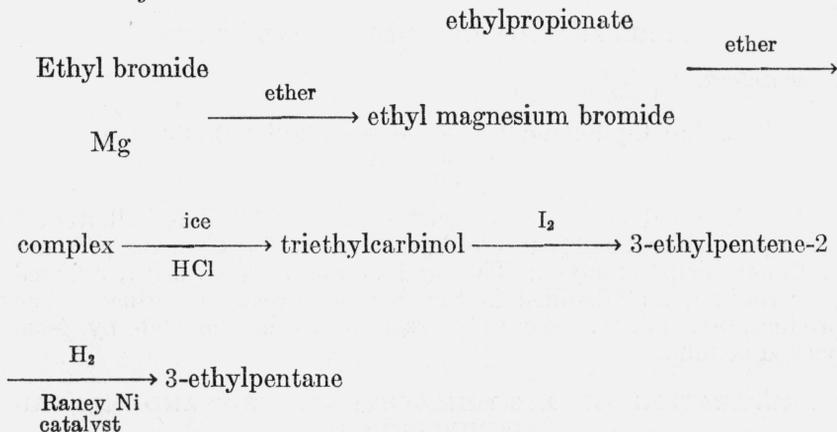
2,3,3-Trimethylbutanol-2 was prepared by the action of acetone on *tert*-butyl magnesium chloride in dry ether in yields up to 30 per cent. The product was recovered, dehydrated to 2,3,3-trimethylbutene-1, and hydrogenated to 2,2,3-trimethylbutane in a manner essentially the same as that described hereinafter for the preparation of 3-ethylpentane. The carbinol boiled at 129° to 133° C, the olefin at 76° to 78° C, and the paraffin at 80° to 82° C in the preliminary separations.

A portion of the 2,3,3-trimethylbutene-1 was purified by distillation through the 150-plate bubble-cap column. From 3,000 ml of crude olefin 2,600 ml of 2,3,3-trimethylbutene-1 was recovered, which was constant-boiling (within 0.01° C) and which had a constant refractive index.

All 2,2,3-trimethylbutane was carefully washed with sulfuric acid, water, sodium bicarbonate solution, dried over calcium chloride, and distilled from sodium. The distillate boiling at 80° to 82° C was fractionated in the 600- by 4-cm packed column. Six liters of material was prepared in this way, fractions of which differed in boiling point by no more than 0.013° C and which had refractive indices (n_D^{20}) of 1.3892 to 1.3894.

5. PREPARATION OF 3-ETHYLPENTANE

Flow diagram:



Triethylcarbinol was made in 80- to 85-percent yield by the action of ethyl propionate on ethyl magnesium bromide in dry ether. The carbinol was isolated from the reaction mixture by decomposing the Grignard complex with ice and dilute hydrochloric acid, and extracting the aqueous layer with ether. The ether solution was distilled through a 100- by 2-cm packed column. The carbinol boiled at 140° to 142° C.

The 3-ethylpentene-2 was formed in a 94-percent yield when triethylcarbinol was slowly distilled in the presence of 0.5 percent of its weight of iodine. The product was dried with calcium chloride, refluxed over sodium, and distilled in the 100- by 2-cm column. The fraction which boiled at 95° to 97° C was collected for hydrogenation.

The 3-ethylpentane was formed in a 97-percent yield when 3-ethylpentene-2 was hydrogenated at 120° C and 1,800 to 2,200 lb/in.² pressure in the presence of Raney nickel catalyst. The product was thoroughly washed with concentrated sulfuric acid, water, 5-percent aqueous sodium bicarbonate, and finally washed several times with water. It was dried with calcium chloride, refluxed over sodium, and distilled through the 100- by 2-cm. column. The fraction which boiled between 92° and 94.5° C was collected for further purification. A total of 2,650 ml was prepared in this way.

The material was further purified by careful fractionation in the 600- by 4-cm packed column. Each fraction was withdrawn after the temperature at the head of the column (corrected to 760 mm Hg) had become constant. In this way 1,750 ml of hydrocarbon was collected at still head temperatures within a range of 0.012° C. All fractions of this portion had a refractive index (n_D^{21}) of 1.3928.

6. ISOLATION OF 2,3,4-TRIMETHYLPENTANE

This octane was prepared by fractionation of a mixture of isomeric octanes supplied through the kindness of Gustav Egloff, of the Universal Oil Products Co. The isomeric octanes were first distilled in a batch still having a 240- by 4-cm column packed with locket chain. Fractions of about 4.5 liters so obtained were distilled in a 150-plate bubble-cap still, recombined according to refractive index, and redistilled.

7. PURIFICATION OF *n*-HEPTANE AND 2,2,4-TRIMETHYLPENTANE

Samples from the purest batches of certified *n*-heptane (California Chemical Co.) and "isooctane" (2,2,4-trimethylpentane) (Röhm & Haas Co., Inc.) were carefully fractionated in a 150-plate bubble-cap column.

IV. DETERMINATION OF PHYSICAL PROPERTIES

The apparatus and technique employed in the measurements of physical properties have already been described in the first report [1] of this series.

In previous work [1, 6, 7] it has been found that data obtained in the distillation of a sample through the 10-in. jacketed column used in determining the boiling point of the sample furnished a rough index of its purity. The distillation data on each sample were obtained at two or more total pressures differing by 7 to 28 mm Hg, one of these values being close to 760 mm Hg. From the rate of change of temperature with pressure so found, the data obtained when the pressure was near 760 mm Hg were corrected to that value. As pressure readings were taken only at intervals during a distillation, minor fluctuations not recorded caused an unevenness in the corrected data amounting to three or four thousandths of a degree. The corrected distillation data obtained in the present work are plotted in figures 2 to 9 and 11 to 13.

The two lower-boiling hexenes, 3,3-dimethylbutene-1 and 2,3-dimethylbutene-1, figures 2 and 3, appear to be of fairly high purity. By comparison, the 2,3-dimethylbutene-2, figure 4, is of very low purity.

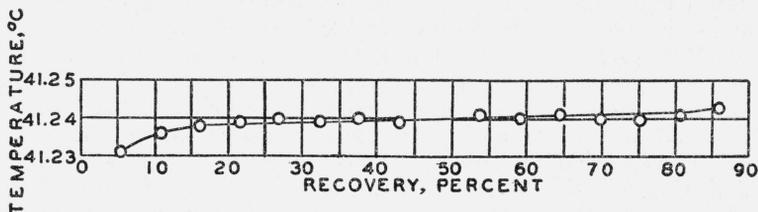


FIGURE 2.—Distillation of 3,3-dimethylbutene-1.

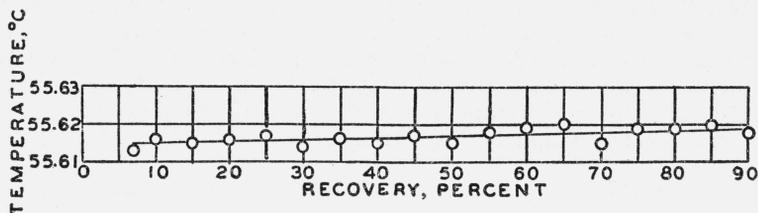


FIGURE 3.—Distillation of 2,3-dimethylbutene-1.

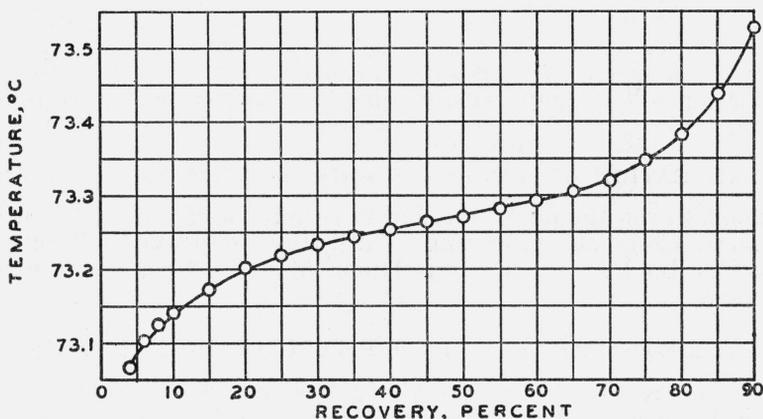


FIGURE 4.—Distillation of 2,3-dimethylbutene-2.

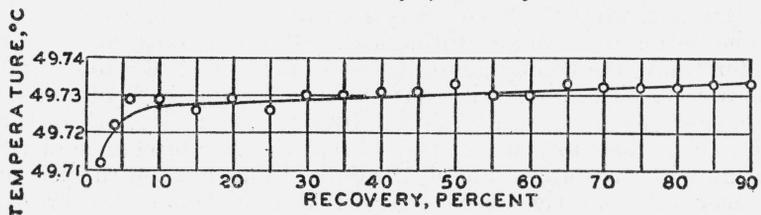


FIGURE 5.—Distillation of 2,2-dimethylbutane.

The two dimethylbutanes, figures 5 and 6, are of about as high purity as the lower-boiling hexenes. The 3-ethylpentane, figure 7,

is of very high purity, no rise of temperature being observed during distillation from 6 percent to 90 percent recovered.

The 2,3,3-trimethylbutene-1, figure 8, appears to be of lower purity than the hexenes. Its paraffin homologue, 2,2,3-trimethylbutane, figure 9, like the 3-ethylpentane, shows no rise of temperature in distillation above 3 percent recovered. A freezing-point determina-

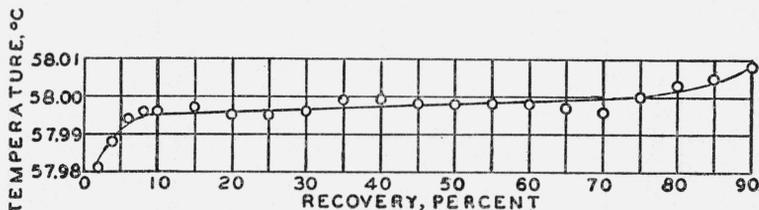


FIGURE 6.—Distillation of 2,3-dimethylbutane.

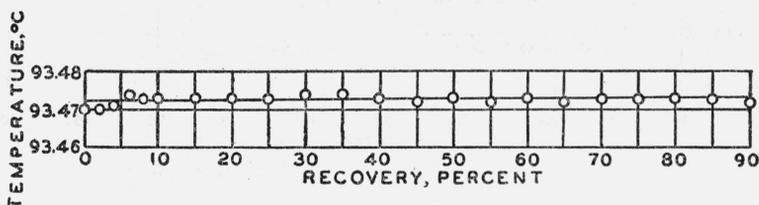


FIGURE 7.—Distillation of 3-ethylpentane.

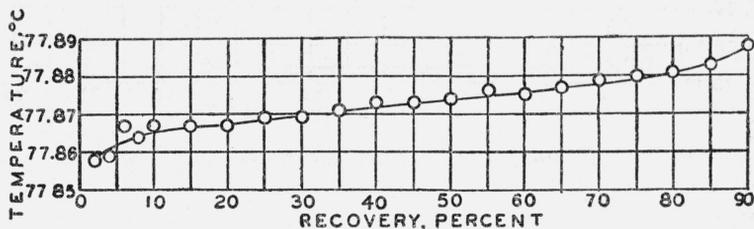


FIGURE 8.—Distillation of 2,3,3-trimethylbutene-1.

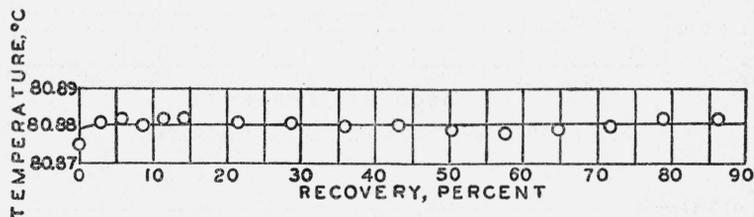


FIGURE 9.—Distillation of 2,2,3-trimethylbutane.

tion on this material is plotted in figure 10. A freezing-point determination on another sample, to which 2 percent of normal heptane had been added, showed the lowering to be 2.17° C per mole-percent of impurity.

The distillation curves of normal heptane, figure 11, and of 2,2,4-trimethylpentane, figure 12, offer no especial points of interest. Figure 13, the distillation curve of 2,3,4-trimethylpentane, is of interest in

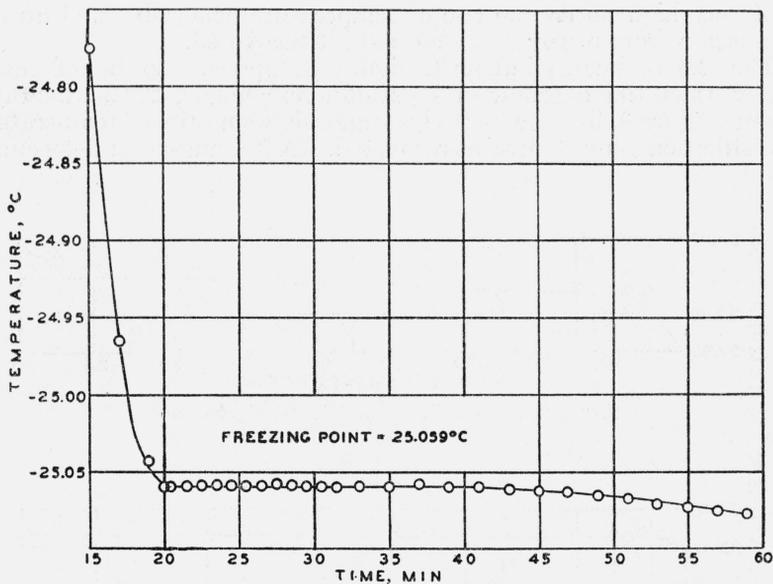


FIGURE 10.—Freezing curve of 2,2,3-trimethylbutane.

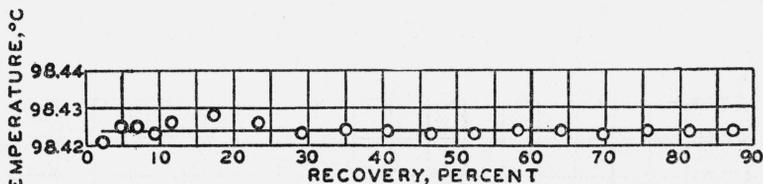


FIGURE 11.—Distillation of n-heptane.

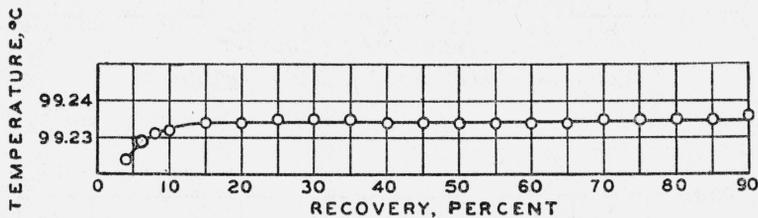


FIGURE 12.—Distillation of 2,2,4-trimethylpentane.

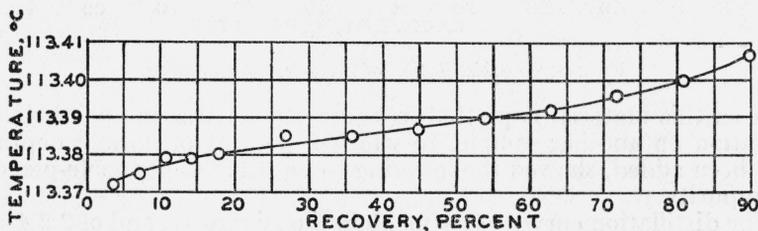


FIGURE 13.—Distillation of 2,3,4-trimethylpentane.

that this material was isolated by fractional distillation from a synthetic crude containing 5 to 10 percent of hexanes and heptanes, the balance being octanes including the four trimethylpentanes, at least two dimethylhexanes, and small amounts of unidentified octanes. Without recourse to fractional crystallization, a product was obtained, 80 percent of which distilled within a range of 0.03°C . The freezing and melting curves of 2,3,4-trimethylpentane are shown in figure 14.

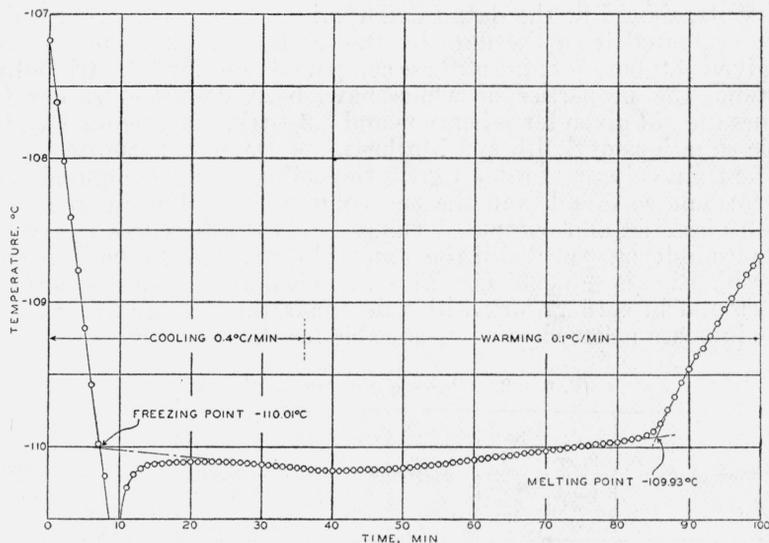


FIGURE 14.—Freezing and melting curves of 2,3,4-trimethylpentane.

TABLE 1.—Boiling-point data on 2,2,3-trimethylbutane

Barometric pressure	Observed boiling point	Computed boiling point	Difference, observed - computed
<i>mm Hg</i>	<i>° C</i>	<i>° C</i>	<i>deg.</i>
740.74	80.006	80.005	+0.001
750.20	80.434	80.436	-.002
758.67	80.819	80.819	.000
764.41	81.082	81.076	+.006
767.44	81.207	81.211	-.004

▪ This value was obtained on a sample from a different batch of 2,2,3-trimethylbutane.

TABLE 2.—Empirical constants in vapor pressure equations

Compound	A	B
3,3-Dimethylbutene-1.....	17.04606	3,274
2,3-Dimethylbutene-1.....	17.18944	3,471
2,3-Dimethylbutene-2.....	17.63641	3,812
2,3,3-Trimethylbutene-1.....	16.96984	3,628
2,2-Dimethylbutane.....	17.06023	3,367
2,3-Dimethylbutane.....	17.19986	3,499
2,2,3-Trimethylbutane.....	17.01002	3,674
3-Ethylpentane.....	17.45112	3,966
2,2,3-Trimethylpentane.....	17.13021	4,020
2,3,4-Trimethylpentane.....	17.25410	4,105

Boiling-point determinations were made on 2,2,3-trimethylbutane at several barometric pressures, the values being given in the first two columns of table 1. Since the heat of vaporization could be assumed to be constant over the small range of temperatures shown in the second column of the table, the equation

$$\log p = A - B/T, \quad (1)$$

where p = pressure; T = absolute temperature; and A , B = empirical constants, should fit the data satisfactorily. The constants A and B were evaluated from the data by the method of least squares, and are given in table 2 for nine of these compounds and for 2,2,3-trimethylpentane, the properties of which have been described earlier [1]. Values are not given for n -heptane and 2,2,4-trimethylpentane, as the cubic equations of Smith and Matheson [9] are more accurate.

The third column of table 1 gives the boiling points computed from the formula so found, and the last column shows the difference between observed and computed values. These differences are of the magnitude to be expected if the standard deviation of a boiling-point determination is $\pm 0.003^\circ \text{C}$. This value is only one-third as large as that found in earlier work with this apparatus [7]. Refinements in technique are believed to be responsible for the reduction.

TABLE 3.—*Properties of preparations*^a

Compound	Freezing point	Boiling point at 760 mm Hg	dI/dP	Refractive index		dn/dt (20° to 25° C)	Density		dD/dt (20° to 25° C)
				n_D^{20}	n_D^{25}		20° C	25° C	
3,3-Dimethylbutene-1	$^\circ \text{C}$	$^\circ \text{C}$	deg/mm Hg			per deg	g/ml	g/ml	g/ml deg
	{ -115.53 -114.7	{ 41.239 41.2	0.0397	1.37604 <i>1.37660</i>	1.37295	-0.000618 -0.000593	0.65293 .65198	0.64786	-0.001014 -0.000908
2,3-Dimethylbutene-1	{ -140.1 -129 to -123	{ 55.615 55.8	.0410	1.39022 <i>1.3915</i>	1.38724	-0.000596	.67801 .6825	.67322	-0.000958
	{ -75.4 -74.2	{ 73.24 73.9	.0414	1.4121 <i>1.4116</i>	1.4092	-0.00057	.7088 .7054	.7045	-0.00086 -0.000580
2,3-Dimethylbutene-2	{ -111.40 -118.8	{ 77.874 78	.0447	1.40292 <i>1.402</i>	1.40004	-0.000576	.70501 .7029	.70054	-0.000890 -0.00116
	{ -100.06 -98.2	{ 49.731 49.7	.0407	1.36864 <i>1.36887</i>	1.36592	-0.000543 -0.000541	.64902 .64944	.64432	-0.000940 -0.000915
2,3-Dimethylbutane	{ -129.79 -123.8	{ 57.999 58.0	.0412	1.37490 <i>1.37499</i>	1.37212	-0.000556 -0.000540	.66150 .66201	.65699	-0.000921 -0.000869
	{ -25.059 -25.0	{ 80.879 80.8	.0449	1.38947 <i>1.38943</i>	1.38683	-0.000528	.69000 .69014	.68576	-0.000848 -0.000820
3-Ethylpentane	{ -118.65 -118.8	{ 93.473 93.3	.0446	1.39337 <i>1.3937</i>	1.39084	-0.000506	.69818 .69860	.69377	-0.000882 -0.000884
	{ -90.60 -90.5	{ 98.424 98.4	$\approx (.0449)$	1.38764 <i>1.38774</i>	1.38511	-0.000506 $\approx .00014$.68368 .68376	.67943	-0.000849 -0.000858
2,2,4-Trimethylpentane	{ -107.37 -107.45	{ 99.233 99.3	$\approx (.0465)$	1.39155 <i>1.39187</i>	1.38915	-0.000480	.69189 .69194	.68778	-0.000822 -0.000844
	{ -109.97 (^c)	{ 113.391 113.4	.0479	1.40431 <i>1.4046</i>	1.40193	-0.000476	.71903 .7195	.71507	-0.000791

^a The values given in the upper row of figures for each compound are those obtained in this work and are believed to be accurate within a few units in the last decimal place given. The lower row of figures (in italics) are taken from Egloff [8] for comparison.

^b Over a wider range of temperatures.

^c At 18° C.

^d Estimated.

^e Probably a typographical error.

^f "Glassy at low temperatures."

^g Copied from reference [7].

The physical properties of the compounds included in this investigation are given in table 3. The upper row of figures for each compound are the values obtained in this work. For comparison, values taken from Egloff [8] are given below in italics. The boiling point of each compound at 760 mm Hg barometric pressure was found by substituting in eq 1 the observed data for the compound, evaluating the constants A and B , and solving the resulting formula for $p=760$. The values so obtained deviate from those shown in figures 2 to 9 and 11 to 13 by one or two thousandths of a degree, the latter having been corrected to 760 mm Hg by linear interpolation only. Refractive indices and densities were obtained at temperatures close to 20° and 25°C and were corrected to 20° and 25° C by assuming the variations with temperature to be linear. All weighings made in the density determinations were corrected to vacuum.

V. REFERENCES

- [1] Donald B. Brooks, Frank L. Howard, and Hugh C. Crafton, Jr., *J. Research NBS* **23**, 637 (1939) RP1259.
- [2] Johannes H. Bruun, *Ind. Eng. Chem., Anal. Ed.*, **8**, 224 (1936).
- [3] *Organic Syntheses*, collective vol. 1, p. 448 (1932). (John Wiley & Sons, New York, N. Y.)
- [4] *Organic Syntheses*, collective vol. 1, p. 451. (John Wiley & Sons, New York, N. Y.)
- [5] P. L. Cramer and A. L. Glasebrook, *J. Am. Chem. Soc.* **61**, 230 (1939).
- [6] Donald B. Brooks, Robetta B. Cleaton, and Frank R. Carter, *J. Research NBS* **19**, 319 (1937) RP1027.
- [7] Donald B. Brooks, *J. Research NBS* **21**, 847 (1938) RP1160.
- [8] Gustav Egloff, *Physical Constants of Hydrocarbons*, vol. 1 (Reinhold Publishing Corp., New York, N. Y., 1939.)
- [9] Edgar Reynolds Smith and Harry Matheson, *J. Research NBS* **20**, 641 (1938) RP1097.

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