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PHYSICAL PROPERTIES OF PURIFIED 2,2,3-TRIMETHYLPENTANE

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ABSTRACT

A sample of 2,2,3-trimethylpentane prepared synthetically was purified by fractionation in an automatically controlled 6-m helix-packed column. The resulting product was of such purity that a good freezing point could be obtained. The freezing point and melting point were determined in an apparatus in which the rate of cooling or heating could be accurately controlled. Other properties measured included the boiling point and its variation with pressure, and refractive index and density and their variations with temperature.

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I. INTRODUCTION

In connection with an investigation of paraffin hydrocarbons as aviation fuel constituents 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, a sample of 2,2,3-trimethylpentane was prepared synthetically, and purified by fractionation in an automatically controlled 6-m helix-packed column. The resulting product was of such purity that a good freezing point could be obtained.

II. PREPARATION OF 2,2,3-TRIMETHYLPENTANE

Methylethyl-*tertiary*-butylcarbinol was prepared from *tertiary*-butyl chloride and methylethylketone, by the Grignard reaction, in yields varying from 21 to 28 percent. *Tertiary*-butyl chloride was obtained from the Eastman Kodak Co., magnesium and ether from the Mallinckrodt Chemical Works, and methylethylketone from Eimer and Amend. All materials were used without further purification. The carbinol distilled at 74° to 76° C at 40-mm Hg pressure.

Methylethyl-*tertiary*-butylcarbinol was refluxed with about 0.5 percent of iodine, and the mixture of resulting olefins was recovered by distillation, dried with calcium chloride, and refluxed with sodium and fractionated in a 100- by 2-cm column packed with Pyrex helices. The portion boiling from 107° to 114° C was collected, and apparently

contained the two isomeric compounds, 2,2,3-trimethylpentene-3, 80 percent, and 2,3,3-trimethylpentene-1, 20 percent, as found by Whitmore and Laughlin [1].¹

The mixture of olefins was hydrogenated at a hydrogen pressure of 2,000 lb/in.² at 130° C in the presence of Raney nickel catalyst. The product was washed with concentrated sulfuric acid, water, 5-percent sodium bicarbonate solution, and then three times with water. It was then dried over calcium chloride, distilled from sodium, and fractionated in a 600- by 4-cm column packed with Pyrex helices. The total charge was 1,700 ml. The still was operated under total reflux until the head temperature, which was measured with a platinum-resistance thermometer, had become constant within 0.01° C. A fraction was then taken by drawing off the 78 ml of liquid in the reflux receiver, and the process was repeated. Distillation data and the refractive indices of the fractions are given in table 1. On the basis of the distillation data, fraction 8 was considered the purest sample of 2,2,3-trimethylpentane, and its physical constants were measured. The residue (530 ml) was saved for future isolation of 2,3,3-trimethylpentane.

TABLE 1.—*Fractionation data*

| Fraction number | Reflux time | Head temperature | Barometric pressure | Boiling point at 760 mm Hg | Refractive index at 20°C |
|-----------------|--------------|------------------|---------------------|----------------------------|--------------------------|
| | <i>Hours</i> | <i>°C</i> | <i>mm Hg</i> | <i>°C</i> | |
| 1..... | 6.7 | 107.5 | | | 1.4017 |
| 2..... | 4.0 | | | | 1.4024 |
| 3..... | 7.0 | 109.57 | 758.13 | 109.66 | 1.4025 |
| 4..... | 7.0 | 109.61 | 756.98 | 109.76 | 1.4030 |
| 5..... | 6.0 | | | | 1.4030 |
| 6..... | 6.0 | | | | 1.4030 |
| 7..... | 4.0 | 109.78 | 759.25 | 109.82 | 1.4030 |
| 8..... | 8.0 | 109.76 | 759.00 | 109.81 | 1.4029 |
| 9..... | 6.0 | | | | 1.4029 |
| 10..... | 6.0 | | | | 1.4029 |
| 11..... | 6.0 | 109.67 | 757.08 | 109.81 | 1.4029 |
| 12..... | 0.5 | | | | 1.4029 |
| 13..... | .5 | | | | 1.4030 |
| 14..... | .5 | | | | 1.4029 |
| Residue..... | .5 | | | | 1.4050 |

III. APPARATUS

A glass-stoppered Pyrex flask of somewhat over 50-ml capacity was used in determining density. A portion of the neck of this flask was constricted to 2.5-mm diameter, and a line was etched on the neck at the middle of this constricted portion. In making a density determination, the flask was filled above this line and placed in a bath maintained at a constant temperature within $\pm 0.01^\circ$ C. When the meniscus of the liquid in the flask showed no further movement under a microscope, the excess liquid was removed, leaving the meniscus a few tenths of a millimeter above the etched line. The neck of the flask was then aerated to remove liquid film, and the final adjustment was made, by removing liquid with a very fine capillary tube while observing the meniscus under a microscope. The flask was then removed from the bath, immersed in dry acetone, dried, and weighed. The liquid was then removed, the flask dried internally, and again

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

weighed. All weighings were made in a dry atmosphere, using calibrated weights, and were corrected to vacuum. The volume of the flask was similarly determined, using air-free distilled water, at 20° C and at 25° C.

The refractive index of the material was determined on an Abbé refractometer (Valentine) graduated to 0.0001. This instrument was immediately calibrated by measuring the index of refraction of a standard sample of 2,2,4-trimethylpentane [2,3], the refractive index of which was 1.39146 at 20° C.

The boiling point was measured while the sample was being distilled through a 10-inch jacketed column, the jacket being externally heated electrically to a temperature such that slight, and only slight, condensation occurred in the column. A jacket temperature about 3° C below the boiling point of the sample was generally found to be satisfactory. A layer of asbestos and a layer of aluminum foil surrounded the heating coil, it having been found by experience to be necessary to eliminate external radiation. A platinum-resistance thermometer inserted in the column was used for the temperature measurements. Atmospheric pressure was measured on a Fortin-type barometer, graduated to 1 mm Hg, and read by vernier to 0.01 mm Hg. The *ensemble* was calibrated each day by measuring the boiling point of distilled water. Earlier work [3] showed that with this procedure the reproducibility averaged about 0.009° C. It is believed that subsequent improvements in technique have materially reduced this error.

The freezing-point determinations were made by means of the apparatus described in a former paper [3], which was modified to facilitate control of the rate of cooling. A Pyrex tube on which had been wound 160 ohms of No. 32 Calido resistance wire was placed inside the Dewar flask, which was immersed in liquid air. The voltage applied to the resistance wire was controlled in the range 15 to 30 volts by a variable transformer and was measured by a voltmeter graduated to 0.2 volt. By this means it was possible to preselect accurately at -110° C any rate of temperature change from 0.8° C per minute cooling to over 1.5° C per minute heating. Tests have shown that with this device a cooling rate of 0.12° C per minute could be maintained with a deviation averaging less than 2 percent and not exceeding 5 percent. Although independently devised, this apparatus is similar in principle and in performance to that described by Roper [5].

A Mueller bridge having coils maintained continuously at 35° C and reading directly to 0.0001 ohm was used in conjunction with the 25-ohm platinum-resistance thermometer on both boiling- and freezing-point tests. Both the bridge and the thermometer were calibrated frequently, the latter in accordance with the procedure specified for the International Temperature Scale.

IV. PHYSICAL PROPERTIES

The distillation data obtained on the sample in one of the two boiling-point determinations, and corrected to a pressure of 760 mm Hg, are shown in figure 1. Taking as the boiling point the average of the temperatures observed in readings from 20 to 80

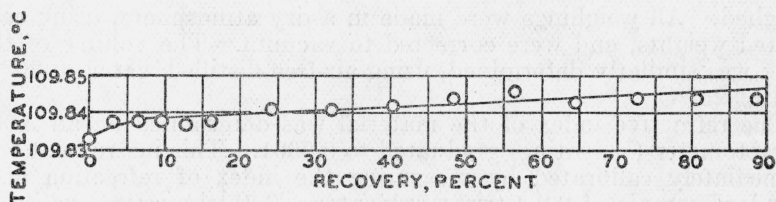


FIGURE 1.—Distillation of purified 2,2,3-trimethylpentane.

percent distilled, the values for the two determinations were as follows:

| Observed boiling point | Barometric pressure |
|------------------------|---------------------|
| °C | mm Hg |
| 109.794 | 758.99 |
| 109.451 | 751.88 |

The value of dT/dP was computed from the equation

$$\log P = A - B/T,$$

the constants A and B being evaluated from the data given above.

Figure 2 shows one of the freezing and melting curves obtained for the sample of 2,2,3-trimethylpentane. Considerable uncertainty

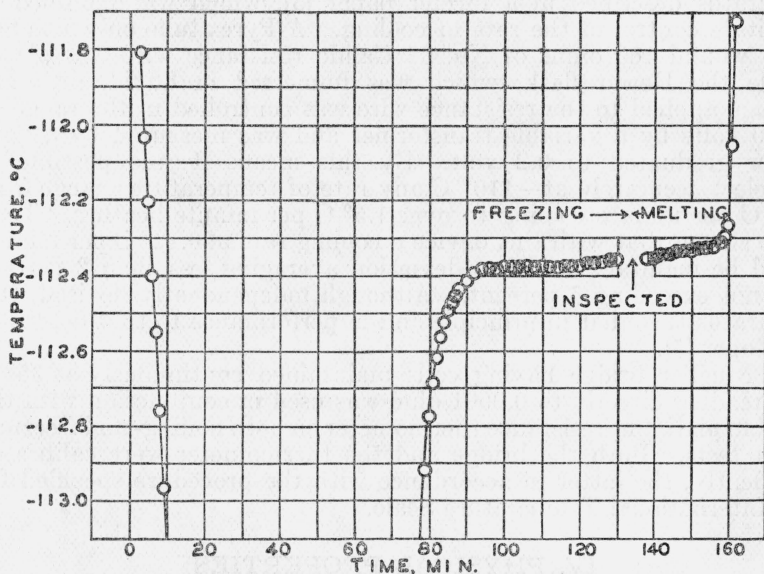


FIGURE 2.—Freezing and melting curves of purified 2,2,3-trimethylpentane.

exists as to the freezing point, since it was necessary to undercool the sample several degrees for about $1\frac{1}{2}$ hours before it would freeze. The values obtained for the freezing points were -112.36° and -112.38° C, and for the melting points -112.34° and -112.31° C.

Refractive-index measurements at two temperatures gave 1.40316 at 19.38° C and 1.40005 at 25.67° C. Density measurements were made at 20° C and 25° C.

Properties of 2,2,3-trimethylpentane calculated where necessary to standard conditions are given in table 2, together with values for comparison taken from Egloff's critical review [4] of the literature.

Owing to the fact that the refractometer and the barometer were not calibrated when taking the data shown in table 1, the refractive-index and boiling-point values given in the two tables differ slightly.

TABLE 2.—Physical properties of 2,2,3-trimethylpentane

| Reference | Melting point | Boiling point at 760 mm Hg | $\frac{dT}{dP}$ | Refractive index | | $\frac{dn}{dt}$ | Density | | $\frac{d\rho}{dt}$ |
|---------------------------|-------------------------------|----------------------------|-----------------|------------------|------------|-----------------|-------------|-------------|--------------------|
| | | | | n_D^{20} | n_D^{25} | | ρ^{20} | ρ^{25} | |
| | °C | °C | deg/mm Hg | | | per deg | g/ml | g/ml | g/ml deg |
| Present work ^a | -112.32 | 109.843 | 0.0480 | 1.40285 | 1.400038 | -0.000494 | 0.71617 | 0.71218 | -0.000797 |
| Egloff [4] | "Glassy at low temperatures." | 110.3 | ----- | 1.4032 | ----- | ----- | .7162 | ----- | ----- |

^a The uncertainty of each value is believed not to exceed a few units in the last decimal place given.

V. REFERENCES

- [1] F. C. Whitmore and K. C. Laughlin, *J. Am. Chem. Soc.* **54**, 4011 (1932).
- [2] Donald B. Brooks, Robetta B. Cleaton, and Frank R. Carter, *J. Research NBS* **19**, 319 (1937) RP1027.
- [3] Donald B. Brooks, *J. Research NBS* **21**, 847 (1938) RP1160.
- [4] Gustav Egloff, *Physical Constants of Hydrocarbons*, **1**, 55 (Reinhold Publishing Corporation, New York, N. Y., 1939).
- [5] Edwin E. Roper, *J. Am. Chem. Soc.* **60**, 1693 (1938).

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