#### **RP482**

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# THE SYNTHESIS, PURIFICATION, AND CERTAIN PHYSI-CAL CONSTANTS OF THE NORMAL HYDROCARBONS FROM PENTANE TO DODECANE, OF *n*-AMYL BROMIDE AND OF *n*-NONYL BROMIDE<sup>1</sup>

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#### ABSTRACT

The normal paraffin hydrocarbons from pentane to dodecane, *n*-amyl bromide and *n*-nonyl bromide have been synthesized and prepared in very pure condition. The boiling points, freezing points, and refractive indices  $(N_D^{25})$  of these compounds have been measured and the values compared with those obtained by other investigators on hydrocarbons isolated from petroleum. Two crystalline modifications of *n*-nonyl bromide freezing at -29.06° and -30.71° C., respectively, were discovered.

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	Introduction

#### I. INTRODUCTION

An investigation on the electrical properties of insulating liquids in progress at this bureau necessitated the preparation of some very pure hydrocarbons. The normal paraffin hydrocarbons were selected because the resistivities of liquids in this series are among the highest known, and because an interpretation of the electrical properties of liquids in terms of molecular structure should be more readily accomplished with their simple molecules than with molecules of more complex structure. All the members of this series from pentane to dodecane were prepared. An examination of the literature when this work was begun showed that many of the physical properties of these substances were not well established. Recently, however, Shepard, Henne, and Midgley (1) <sup>2</sup> isolated these hydrocarbons in a high degree

<sup>&</sup>lt;sup>1</sup> This work is part of an investigation on the electrical properties of insulating liquids which is being carried on in cooperation with the Utilities Research Commission (Inc.), Chicago, Ill. <sup>2</sup> The figures in parentheses here and throughout the text relate to the bibliography at the end of this paper.

In addition to the hydrocarbons, two of the intermediates in their preparation, *n*-amyl bromide and *n*-nonyl bromide, were obtained in a pure condition and certain of their physical constants measured. Nonyl bromide in particular proved interesting since it was found to exist in two crystalline modifications, a fact not previously recorded.

#### II. METHODS

The methods used in the purification, in the determination of purity, and in the measurement of the physical constants were similar for all the hydrocarbons and are referred to frequently in discussing the individual substances. It is therefore advisable to describe these methods briefly at this point before proceeding to a more detailed description of the individual syntheses and purifications.

#### 1. PURIFICATION

The physical methods employed were fractional distillation and fractional crystallization. Apparatus and methods for efficiently pursuing these processes have been developed in this bureau, and were used with only minor modifications. The liquids were distilled through a 10-plate bubble cap fractionating column (2, 3) fitted with a variable reflux regulator of the type described by Marshall (4). The reflux ratio during the final distillation was always greater than 10:1.The distillation range was read on a thermometer extending into the vapor from the top of the column. The method employed in fractional crystallization (5) was to transfer the frozen material to a vacuum funnel, stir it to a mush, and draw off the mother liquor with For the liquids whose freezing points were higher than that suction. of decane, melting took place so slowly that a vacuum funnel was unnecessary. In the case of decane, the crystals were separated from the mother liquor in a centrifuge designed for use at low temperatures by Hicks-Bruun and Bruun (6).

## 2. FREEZING POINT DETERMINATIONS

The freezing point determinations were made with a glass-incased, 25.5 ohm (at the ice point), potential terminal, platinum resistance thermometer of the strain-free type, using as accessories a Mueller thermometer bridge and commutator. The thermometer was calibrated by the heat division of this bureau.

The sample was contained in a double-walled Pyrex tube. By varying the air pressure in the annular space of this double walled tube, any desired rate of cooling could be obtained. This vessel was about 11 inches in length and was filled to a depth of 8½ inches with the liquid in question. With the thermometer in place, the liquid extended 4 inches above the resistance coil. The liquid could be stirred vigorously by means of a spiral of nickel chromium wire which surrounded the thermometer. After the sample (about 70 ml) had been introduced and the thermometer and stirrer adjusted in place, a thin brass tube (as a safety measure) was fitted over the vessel, which was then immersed in liquid air. Freezing took place from the walls toward the center. Stirring was possible until the sample was about half frozen. A change in the slope of the cooling curve was noticed (particularly if the sample was impure) as soon as stirring stopped. This may be explained on the supposition that equilibrium conditions were no longer maintained, and the impurities crystallized simultaneously with the pure substance. The freezing point of any liquid was taken as the temperature at which the cooling curve (figs. 2 to 11) became approximately horizontal. The principal criterion of purity was the slope of this approximately horizontal portion of the freezing point curve.

Considerable precision was attained with these arrangements. Duplicate experiments were made with hexane, octane, decane, and dodecane, and in no instance was a variation greater than 0.002° C. in the freezing point obtained.

An examination was made of the thermometric technique in order to determine how accurately the measured temperatures agreed with the international scale of temperature. The question of conduction through the leads was studied by varying the height of the liquid above the resistance coil. Determinations of the freezing point of hexane in which this height was varied from 5 to 2 inches agreed within 0.001° C., and indicated that with the apparatus in question this effect was negligible. For the thermometer regularly used, the values of the constants given by the heat division of this bureau permitted the calculation of the temperature with an accuracy of 0.02° C. In order to obtain a further test on the accuracy of this thermometer and accessories, freezing-point determinations were made on two samples, using the equipment of the low-temperature laboratory of this bureau, with the assistance of R. B. Scott. The values  $-56.82^{\circ}$  and  $-95.36^{\circ}$  C. obtained on samples of octane and hexane with the equipment of the low-temperature laboratory compare well with the values  $-56.82^{\circ}$  and  $-95.37^{\circ}$ C., which had been obtained on these samples with the regular equipment. Thus with two different thermometers, bridges, and operators the maximum discrepancy was 0.01° C. It seems reasonable to conclude that the thermometric measurements do not differ from the international scale by more than  $\pm 0.02^{\circ}$  C.

### 3. BOILING-POINT DETERMINATIONS

The boiling points were determined with the aid of a platinum resistance thermometer in the apparatus shown in Figure 1. Vapor given off from the boiling liquid in the flask had, first, to pass through liquid in the bubble cap before reaching the thermometer, thus preventing superheating. The outer jacket was electrically heated sufficiently to permit the liquids with high boiling points to distill over, but was always kept somewhat below the boiling temperature. About half of the 50 ml sample was distilled over during a boiling-point determination. The temperature generally rose less than 0.01° C. except during the distillation of the first few milliliters when the thermometer was warming up. Barometric pressures within 0.02



# FIGURE 1.—Boiling-point apparatus

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mm were obtained immediately before and after the boiling-point reading from the aeronautic-instruments section of this bureau. The boiling points of the hydrocarbons were corrected to 760 mm with the aid of the values given by Shepard, Midgley, and Henne (1) for  $\frac{dt_B}{dp}$ , the rate of change of boiling point with change of pressure. For *n*-amyl bromide several boiling-point determinations in the vicinity of 760 mm were used to compute  $\frac{dt_B}{dp}$ . Duplicate boilingpoint determinations were made in most cases and agreed within 0.01° C.

# 4. REFRACTIVE INDEX DETERMINATIONS

Refractive indices were measured by L. W. Tilton, of the optical instruments section of this bureau, with three different Abbe refractometers. Each was calibrated with distilled water and with several prismatic standards of refractivity whose indices had been previously measured on a spectrometer by the method of minimum deviation (7). The observations on these liquids were made at water jacket temperatures of 25° C. in a room the temperature of which was between 23° and 24° C. On each instrument two series of measurements were made in which the liquids were sampled in the direct and also in the reverse order of their optical densities. Each of these samplings consisted of two successive applications of liquid to the refractometer block by means of a clean glass rod, and the instruments were set and read twice after each application.

The precision of these refractive index readings is characterized by probable errors of a few units in the fifth decimal place. With instruments so calibrated an accuracy of  $\pm 5 \times 10^{-5}$  is attainable when using solid samples. With liquids, however, the accuracy may be affected by contamination of the small samples when they come in contact with the cement which holds the refractometer block in its water jacket. Also, the high volatility of some of the samples of lower index causes them to cool appreciably and, perhaps, to maintain a temperature lower than that indicated by the thermometer which is immersed in the jacketing stream. In accord with this supposition the results on the different refractometers do not agree as well for the liquids having the lower indices. In no case, however, does the index as determined by any one refractometer depart from the mean recorded in Table 1 by more than  $\pm 12 \times 10^{-5}$ , the average of such departures being  $\pm 3 \times 10^{-5}$ .

# III. SYNTHESIS AND PURIFICATION

The synthesis and purification of the hydrocarbons and some of their intermediate products are described in the following paragraphs.

#### 1. *n*-PENTANE

The Sharples Solvent Corporation, of Philadelphia, kindly supplied a gallon of amyl alcohol for this preparation. This material was stated by them to be a mixture of 2-pentanol and 3-pentanol with not more than 1 per cent of tertiary amyl alcohol and possibly a trace of diamylene. Fractional distillation yielded a large middle fraction boiling between 116.4° and 118.4° C., which was undoubtedly a mixture of 2 and 3 pentanol. Both of these substances on dehydration and subsequent hydrogenation yield *n*-pentane. The dehydration was performed with the use of sulphuric acid exactly as described in Organic Syntheses (8). The pentenes thus obtained were fractionated and the portion which distilled between  $35.8^{\circ}$  and  $36.4^{\circ}$  C. was retained. The pentenes were then hydrogenated by passage through a reaction tube filled with nickel catalyst maintained at 140° C. Practically complete reduction took place in one passage.



FIGURE 2.—n-pentane cooling curve

sulting pentane was shaken three times with concentrated sulphuric acid, then washed twice with a 10 per cent solution of sodium carbonate, and finally with water. After drying with calcium chloride, the pentane was fractionally distilled three times. About 750 ml boiling over a range of 0.03° C. was collected as pure material. An examination of the freezing point curve (fig. 2) indicates the high purity of the sample. The material froze between  $-129.735^{\circ}$  and  $-129.761^{\circ}$  C., a range of 0.026° C.

#### 2. n-HEXANE

The starting material in this synthesis was n-propyl alcohol. It was converted into the bromide by the hydrobromic-sulphuric acid



FIGURE 3.—n-hexane cooling curves

method (9). The bromide was then converted into hexane by treatment with sodium shot, using the method employed by Faillebin (10). The last traces of *n*-propyl bromide were removed by refluxing the crude hexane with liquid sodium potassium alloy for four hours. The hexane was then shaken with cold concentrated sulphuric acid until the acid layer was colorless, then shaken with a 10 per cent solution

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of sodium carbonate, then with water, and finally dried with anhydrous calcium chloride. This material was fractionally distilled thrice, and 1,500 ml which distilled within 0.04° C., was obtained. It was collected in two nearly equal fractions which showed a pronounced difference in freezing behavior, although distilling within 0.04° C. (Fig. 3.) The second fraction (Curve II) gave a more nearly horizontal curve and froze 0.12° C. higher than the first fraction. (Curve III.) A 400-ml portion of the second fraction was stirred with 175 ml of chlorosulphonic acid at 45° C. for seven hours. (This reagent has been reported as efficacious in the removal of branch chain hydrocarbons (11, 12).) After washing thrice with a 10 per cent solution of sodium hydroxide and once with water, the sample was dried with calcium chloride and again distilled. The freezing range of this sample as shown in Curve I (-95.342° to -95.368° C.) was only 0.026° C., and indicated that the hexane was of high purity.

### 3. n-HEPTANE

Several liters of heptane, the original source of which was the Jeffrey pine, was furnished by Graham Edgar, of the Ethyl Gasoline Corporation. This material was of very high purity, as is illustrated



FIGURE 4.—*n*-heptane cooling curves

by its freezing behavior. (Fig. 4, Curve II.) Vigorous treatment with chlorosulphonic acid and subsequent distillation raised the freezing point 0.008° C. Curve I illustrates the freezing behavior of the treated sample. This sample froze from  $-90.619^{\circ}$  to  $-90.628^{\circ}$  C., a range of only 0.009° C., indicative of exceptionally high purity. The same value,  $-90.62^{\circ}$  C., was obtained on a sample of heptane isolated from petroleum by Hicks-Bruun and Bruun (6).

#### 4. n-OCTANE

The starting material in this synthesis was *n*-butyl alcohol. It was converted into the bromide by the hydrobromic-sulphuric acid method (9). The bromide was then converted into octane in a manner similar to that employed by Lewis, Hendricks, and Yohe (13). The procedure was as follows: Sodium in 73 g portions was converted to a finely divided shot by melting and shaking under xylene in a 1-liter 3-necked Pyrex flask. The xylene was decanted and the sodium washed several times with anhydrous ether. It was then covered with 300 ml of anhydrous ether and the flask fitted with a dropping funnel, stirrer with mercury seal, and reflux condenser with calcium chloride tube. The flask was placed in an ice-water bath, the stirrer started, and 384 g of *n*-butyl bromide run in over a period of three hours. The excess sodium was destroyed by running water

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into the mixture. The octane layer was drawn off, and the ether and octane separated by fractional distillation. The impure octane was then refluxed with a 10 per cent solution of sodium hydroxide in alcohol for several hours to destroy any unconverted butyl bromide. Water was then added, and the octane separated from the aqueous layer. It was shaken with cold concentrated sulphuric acid until the acid layer remained colorless; then shaken with a 10 per cent solution of sodium carbonate, then with water, and finally dried over calcium chloride. In this way 3,200 ml of crude material was prepared. It was fractionally distilled four times. At the end of this fractionation, 1,800 ml of material distilling within a range of 0.04° C. was obtained. This material was collected in two equal fractions which had the same freezing point. However, judging from the slope of the freezing-point curve (fig. 5, Curve *III*), it was not yet pure. A sample further purified by three fractional crystallizations froze as shown in Curve *II*. This material, although freezing range.



FIGURE 5.—*n*-octane cooling curves

Another sample was stirred with chlorosulphonic acid at  $45^{\circ}$  C. for seven hours and this treatment repeated with fresh chlorosulphonic acid three times. The octane was separated from the chlorosulphonic acid, washed with a 10 per cent solution of sodium hydroxide, then with water, dried over calcium chloride, and again fractionally distilled. As a result, 270 ml of material was obtained, freezing between  $-56.815^{\circ}$  and  $-56.840^{\circ}$  C., a range of  $0.025^{\circ}$  C., which indicates its high purity.

### 5. n-NONANE AND n-NONYL-BROMIDE

The starting materials in this synthesis were *n*-heptyl bromide and ethylene oxide obtained from Eastman Kodak Co. and from Carbide & Carbon Chemicals Corporation. From these *n*-nonyl alcohol was prepared according to the following reactions:

 $CH_3 (CH_2)_5 CH_2 Br + Mg \longrightarrow CH_3 (CH_2)_5 CH_2 Mg Br$ 

$$CH_3 (CH_2)_5 CH_2 Mg Br + CH_2 - CH_2 \longrightarrow$$

 $CH_3 (CH_2)_7 CH_2 OMg Br \longrightarrow CH_3 (CH_2)_7 CH_2 OH$ 

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This method is exactly analogous to the preparation of *n*-hexyl alcohol from *n*-butyl bromide and ethylene oxide described in Organic Syntheses (14). The *n*-nonyl alcohol was fractionally distilled under a pressure of 83 mm. From the original 1,000 g of *n*-heptyl bromide, 545 ml of *n*-nonyl alcohol distilling between 143.7° and 144° C. was obtained. This purified alcohol was converted into *n*-nonyl bromide by the hydrobromic-sulphuric acid method (9). The resulting product was fractionally distilled at 83 mm and the material distilling between 144.55° and 144.60° C. used in the synthesis of *n*-nonane.

The *n*-nonyl bromide was converted in the usual manner into nonyl magnesium bromide, which was then decomposed with ice and the nonane separated by steam distillation. It was then shaken in turn with concentrated sulphuric acid, 10 per cent sodium carbonate solution, dried over calcium chloride, and fractionally distilled once. A yield of 210 ml of *n*-nonane distilling within a range of 0.03° C. was obtained. The freezing behavior is shown in Figure 6. The freezing range from  $-53.700^{\circ}$  to  $-53.754^{\circ}$  C. was 0.054° C., which is somewhat greater than that obtained for the other hydrocarbons, indicating a less pure material. The freezing point,  $-53.70^{\circ}$  C., is





lower than the value  $-53.68^{\circ}$  C. given by Shepard, Henne, and Midgley (1), and the value  $-53.65^{\circ}$  C. obtained on a sample of very pure nonane isolated by White and Rose (15) from petroleum.

The behavior of *n*-nonyl bromide during its freezing point measurements indicated clearly that two crystalline modifications of this substance exist. Curve I (fig. 7) is a time temperature cooling curve obtained in the usual manner with stirring. The temperature, after remaining constant at  $-30.71^{\circ}$  C. for about seven minutes, rose abruptly to  $-29.06^{\circ}$  C., and again remained approximately constant for a short time. Simultaneously with this rapid temperature change, stirring became much easier. If the liquid was not stirred, crystal-lization occurred at  $-30.71^{\circ}$  C. without the appearance of the  $\beta$ modification. Curves II and III are heating curves, Curve II showing the behavior of a sample which had been frozen with stirring and in which the  $\beta$ -phase had made its appearance, while Curve III shows the behavior of a sample frozen without stirring in which the  $\beta$ -phase had not appeared. These curves show a difference in melting behavior and afford confirmation of the existence of two modifications. The freezing point of the  $\alpha$ -modification is  $-30.71^{\circ}$  C. The freezing point of the  $\beta$ -modification can not be stated so definitely, since it is possible that the approximately flat portion of the Curve (I) is caused by an equality between the loss of heat to the surroundings and the gain in heat caused by the transformation. The freezing point of the  $\beta$ -modification, however, can not be below  $-29.06^{\circ}$  C., and judging from the heating Curve (*III*), it seems improbable that it can be appreciably higher. Moreover, in another time-temperature cooling, experiment, a horizontal portion of the curve was obtained at  $-29.06^{\circ}$  C. Thus it seems probable that  $-29.06^{\circ}$  C. represents the true freezing temperature of the  $\beta$ -modification.



FIGURE 7.—*n*-nonyl bromide I, cooling curve, II and III heating curves

#### 6. n-DECANE AND n-AMYL BROMIDE

The starting material in this synthesis was Eastman's *n*-propyl alcohol. It was converted to *n*-propyl bromide by the hydrobromicsulphuric acid method (9). The resulting bromide was fractionally distilled once. The bromide was then converted to *n*-amyl alcohol by the use of ethylene oxide in a manner exactly analogous to that of the preparation of *n*-hexyl alcohol from *n*-butyl bromide and ethylene oxide, described in Organic Synthesis (14). The *n*-amyl alcohol was fractionally distilled twice and 1,600 ml of material distilling between 137.82° and 137.92° C. obtained. This was converted to the bromide by the hydrobromic-sulphuric acid method (9) and 1,150 ml of the bromide distilling between 129.40° and 129.50° C. obtained. The freezing range of this material (fig. 8) was only 0.014° C. and

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indicated it to be of high purity. This material was used to synthesize decane as follows: Pea-sized sodium pellets were added through a reflux condenser to 100 ml portions of amyl bromide in a 500 ml flask at such a rate that the liquid, which was first heated to boiling, continued to boil gently. After no more sodium could be added (owing to accumulation of solid), the reaction mixture was cooled, treated with water, and the hydrocarbon layer separated and dried with calcium chloride. This process was repeated three times before



FIGURE 8.—n-amyl bromide cooling curve

the amyl bromide was practically completely converted. Finally the decane was refluxed over sodium potassium alloy for six hours to remove the last traces of amyl bromide. The decane was decanted from the alloy and shaken in turn with several portions of cold concentrated sulphuric acid until the acid remained colorless, then shaken with 10 per cent sodium carbonate solution, and finally with water. It was then fractionally distilled once. Practically all the sample of 505 ml distilled between 173.37° and 173.47° C. It was collected in two nearly equal fractions, one between 173.37° and 173.43° C., the other between 173.43° and 173.47° C. The freezing points of these two fractions were  $-29.88^{\circ}$  and  $-29.76^{\circ}$  C., respectively.



FIGURE 9.—*n*-decane cooling curves

The cooling curve for the sample which gave  $-29.76^{\circ}$  C. as the freezing point is shown in Figure 9 (Curve II). Shortly after this sample was obtained Bruun and Hicks-Bruun (16) obtained from petroleum by distillation and by crystallization, with the use of a centrifuge, a decane sample of exceptional purity freezing at  $-29.68^{\circ}$  C. By fractional crystallization with the same centrifuge, the freezing point of the synthetic sample was raised to the identical value  $-29.68^{\circ}$  C. The freezing range from  $-29.680^{\circ}$  to  $-29.692^{\circ}$  C. (Curve I, fig. 9) indicates very high purity.

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#### 7. n-UNDECANE

The starting materials in this synthesis were Eastman's best grade of *n*-heptyl bromide and *n*-butyraldehyde from which 4-undecanol was synthesized as follows: A 50 ml portion of a mixture of 537 g of *n*-heptyl bromide in 900 ml of anhydrous ether was run onto 75 g of magnesium in a 5-liter 3-necked flask, fitted with reflux condenser, stirrer with mercury seal, and dropping funnel. A crystal of iodine was added and the reaction started by warming slightly. The remainder of the heptyl bromide in ether was then dropped in at such a rate that the reaction mixture boiled gently. After all the heptyl bromide had been added, 216 g of butyraldehyde in 200 ml of ether was run in slowly. The reaction mixture was allowed to cool, decomposed with ice and dilute sulphuric acid, filtered through glass wool to remove the magnesium residue, and the 4-undecanol layer separated. This material was fractionally distilled once at 93 mm pressure; 1,230 g of 4-undecanol distilling from 155° to 157° C. was obtained from 3,000 g of *n*-heptyl bromide.

The dehydration of 4-undecanol should yield a mixture of two undecylenes, depending on the manner in which water splits off. Thus

Both of these undecylenes should yield *n*-undecane on hydrogenation.

OH

H

However, the dehydration of 4-undecanol proved to be difficult. Attempts to dehydrate it by heating with 60 per cent sulphuric acid, by refluxing with zinc chloride, by distilling from iodine, and by passing the vapor over aluminium oxide at 350° C., were entirely unsatisfactory and yielded no undecylenes. By running the alcohol into sirupy phosphoric acid at 250° C., a small quantity of undecylene was obtained. Ross and Leather (17) obtained an undecylene from methyl nonyl carbinol by heating the alcohol on a steam bath with phosphorus pentoxide. This method was tried and proved more satisfactory. About 200 ml of 4-undecanol, with 100 g phosphorus pentoxide was placed in a 500-ml flask fitted with a reflux condenser and calcium chloride tube. The flask was then heated for eight The resulting pasty material was extracted hours on a steam bath. with ether and the extract fractionally distilled. In addition to the undecylenes distilling from 191° to 193° C., a considerable quantity of material (almost half) distilled in the range from 222° to 223° C. This material gave the phenylhydrazine test for a ketone. It was probably propyl heptyl ketone and resulted from the oxidizing action of phosphorus pentoxide. This ketone was reduced to 4-undecanol by mixing with an equal volume of amyl alcohol, and adding an excess of sodium in small pieces to the boiling mixture. It was then washed with water, dried, and separated from the amyl alcohol by fractional distillation. It distilled at atmospheric pressure from 228° to 229° C. The 4-undecanol thus obtained was treated with phosphorus pentoxide

or

as before and more undecylene obtained. Altogether 800 ml of undecylene was obtained from 1,230 g of 4-undecanol.

Attempts to hydrogenate the undecylene to undecane by passage over a nickel catalyst at 200° C. were not satisfactory. The first small portion which was collected was almost completely hydrogenated, but the catalyst soon became inactive, presumably owing to poisoning by impurities in the undecylene. The undecylene was, however, satisfactorily hydrogenated by passage over a copper chromite catalyst (18) at 200° C., this catalyst being less readily poisoned than nickel. The undecylenes remaining unconverted were removed by shaking with cold concentrated sulphuric acid. The undecane was washed with a 10 per cent solution of sodium carbonate and dried with calcium chloride. Approximately 700 ml of crude undecane was obtained. This material was quite impure. After four fractional distillations 350 ml was obtained distilling over a range of 0.5° C. Freezing point measurements showed that this material was still quite impure. Fractional crystallization was used for final purification and the progress of purification followed with the platinum resistance thermometer. After many fractional crystallizations 75 ml of



FIGURE 10.—*n*-undecane cooling curve

very pure material was obtained, 75 ml only slightly less pure, and 100 ml of fairly pure material. The freezing range of the purest sample, from  $-25.613^{\circ}$  to  $-25.635^{\circ}$  C., was only  $0.022^{\circ}$  C. and is indicative of high purity. (Fig 10.)

#### 8. *n*-DODECANE

The starting materials in this synthesis were *n*-butyl bromide and ethylene oxide from which hexyl alcohol was synthesized as described in Organic Syntheses (14). The hexyl alcohol resulting was fractionally distilled and the portion distilling between 156° and 157° C. converted into the bromide by the hydrobromic-sulphuric acid method (9). Practically all of this hexyl bromide distilled between 155.20° and 155.32° C.

Dodecane was prepared from the hexyl bromide by the use of sodium in exactly the same manner as decane from amyl bromide. Finally the dodecane was refluxed over sodium potassium alloy for six hours to remove the last traces of hexyl bromide. The dodecane was then decanted from the alloy and shaken with several portions of cold concentrated sulphuric acid until the acid remained colorless, then shaken with a 10 per cent solution of sodium carbonate and finally with water. Two fractional distillations at atmospheric pressure yielded 570 ml of dodecane with a distilling range of  $0.2^{\circ}$ . It had a slightly acrid odor, and evidently contained unsaturated compounds

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caused by cracking at the high temperature necessary to distill at atmospheric pressure. Its freezing behavior indicated that it was not pure. (Fig. 11, Curve II.) After many crystallizations, a 75 ml sample with the freezing behavior shown in Curve I was obtained. This material froze from  $-9.609^{\circ}$  to  $-9.669^{\circ}$ , a range of  $0.06^{\circ}$  C., indicative of a fairly pure material, through probably not as pure as some of the other hydrocarbons obtained.



FIGURE 11.—n-dodecane cooling curves

# IV. COMPARISON OF PHYSICAL CONSTANTS WITH THOSE OF SHEPARD, HENNE, AND MIDGLEY

Physical constants of all the hydrocarbons described in this paper are available in the literature. In general, the criteria of purity were not as strict as those employed in this investigation and the methods of determining the constants, in particular the methods of determining temperature, were not sufficiently refined to yield results of high accuracy. In consequence, the freezing points reported in the literature differ widely. The values obtained on samples isolated from petroleum at this bureau, to which reference has already been made (6, 15, 16) and the values obtained by Shepard, Henne, and Midgley (1) are notable exceptions to this statement. Only Shepard, Henne, and Midgley (1) have recorded values for the entire series from pentane to dodecane. Their values, moreover, were obtained on samples isolated from petroleum, so that a comparison with values on samples obtained in an entirely different manner; that is, by synthesis, is valuable in establishing the true value of the constants. For these reasons only the values of Shepard, Henne, and Midgley (1) are recorded for comparison in Table 1.

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	Boiling point at 760 mm <sup>1</sup>		Freezing point in air		Refractive index $N_D^{25}$	
Substance	Author	Shepard, Henne, and Midgley	Author	Shepard, Henne, and Midgley	Author	Shepard Henne, and Midgley
Pentane. Hexane Heptane Octane. Nonane Decane. Undecane <sup>2</sup> . Dodecane <sup>2</sup> . Amyl bromide. α-Nonyl bromide. β-Nonyl bromide.	°C. .36.06 68.70 98.38 125.59 150.72 174.02 129.58	°C. 36.00 68.71 98.38 125.59 150.71 174.06	$\begin{array}{c} ^{\circ}C.\\ -129.73\\ -95.34\\ -90.62\\ -56.82\\ -53.70\\ -29.68\\ -25.61\\ -9.61\\ -94.67\\ -30.71\\ -29.06\end{array}$	°C. -129.93 -95.39 -90.65 -90.62 <sup>3</sup> -56.90 -53.68 -53.65 <sup>3</sup> -29.76 -29.68 <sup>3</sup> -25.65 -9.73	°C. 1. 35470 1. 37224 1. 38510 1. 39509 1. 40318 1. 40961 1. 41495 1. 41952 1. 41952 1. 44199 1. 45221 1. 45221	°C. 1. 35495 1. 37230 1. 38553 1. 39534 1. 40340 1. 40986 1. 41516 1. 41967

#### TABLE 1.—Physical constants of normal hydrocarbons

<sup>1</sup> The values for  $dt_B/dp$  for the hydrocarbons were taken from the paper by Shepard, Henne, and Midg-ley (1) while that for amyl bromide was determined and found equal to 0.048° /mm. <sup>2</sup> The boiling point of undecane and dodecane and *n*-nonyl bromide were not determined owing to the

probability of some thermal decomposition. <sup>3</sup> Values obtained on samples isolated from petroleum by Hicks-Bruun and Bruun (6) (heptane), White and Rose (15) (nonane), and Bruun and Hicks-Brunn (16) (decane).

The agreement between these two sets of values of physical constants, although somewhat less satisfactory than is to be desired, is nevertheless much superior to that generally obtained by investiga-tors on the physical constants of organic liquids. The greatest discrepancy occurs with pentane in which there is a difference of  $0.06^{\circ}$  in the boiling point and  $0.2^{\circ}$  in the freezing point. The agreement on the boiling points from hexane to nonane is excellent. freezing point agreement is not so satisfactory. With the exception of nonane (which was not quite pure), the freezing point values obtained in this work are all higher than those obtained by Shepard, Henne, and Midgley (1). It is probable that the higher values should be considered the more reliable since impurities, except with one type of solid solution, lower the freezing point. Dodecane, as shown by the slope of the freezing point curve, was not quite pure, and it seems possible that the true freezing point may be still higher than the value recorded here, by from 0.05° to 0.1° C. Unfortunately, sufficient dodecane was not available to continue the fractional crystallization and test this point. The other hydrocarbons were purer than nonane and dodecane and their freezing points are probably correct within  $0.02^{\circ}$  to  $0.05^{\circ}$  C.

The values recorded here for the refractive indices are lower than those given by Shepard, Henne, and Midgley (1). The average value of the differences is  $22 \times 10^{-5}$ .

Refractive indices are not a sensitive test for small amounts of impurities, particularly if the refractive index of the impurity is close to that of the pure substance. Thus 1 per cent of heptane in 99 per cent of octane with refractive indices of 1.38510 and 1.39509, respectively, would give a liquid with refractive index of 1.39499, differing by only  $10 \times 10^{-5}$  from that of pure octane. A calculation based on the differences between the freezing point values given by Shepard, Henne, and Midgley (1), and those recorded here, shows

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that the difference in purity is generally much less than 1 mole per cent. Since the impurities most likely to be present in both cases are isomers, the refractive indices of which do not differ greatly from those of the normal hydrocarbons, it is improbable that the average value for the difference,  $22 \times 10^{-5}$ , can be accounted for by impurities, but instead is attributable to differences in the instruments or methods of measurement.

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